



UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY.DOCKET NO./TITLE	REQUEST ID
14/865,805	09/25/2015	David Ofer	TIA-10103/57	179926

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



UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY.DOCKET NO./TITLE	REQUEST ID
14/865,805	09/25/2015	David Ofer	TIA-10103/57	179928

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



UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE	REQUEST ID
14/865,805	09/25/2015	TIAX LLC	TIA-10103/57	97748

Acknowledgement of Loss of Entitlement to Entity Status Discount

The entity status change request below filed through Private PAIR on 10/15/2019 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 Gould
Registration Number:	59142



UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/865,805	07/12/2016	9391317	TIA-10103/57	1076

25006 7590 06/22/2016
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 0 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;
TIAX LLC, Lexington, MA;
Adrian W. Pullen, Boston, MA;
Suresh Sriramulu, 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
 900 Wilshire Drive, Suite 300
 Troy, Michigan 48084

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.

<i>Ann Andrusik</i>	(Depositor's name)
<i>Ann Andrusik</i>	(Signature)
June 10, 2016	(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/865,805	09/25/2015	David Ofer	TIA-10103/57	1076

TITLE OF INVENTION: POLYCRYSTALLING 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	06/10/2016
EXAMINER		ART UNIT	CLASS-SUBCLASS			
P. F. Godenschwager		1767				

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,
- (2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

- 1 Dinsmore & Shohl LLP
- 2 Weston R. Gould
- 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./

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

Date June 10, 2016

Registration No. 59,142

Electronic Patent Application Fee Transmittal

Application Number:	14865805			
Filing Date:	25-Sep-2015			
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-10103/57			
Filed as Small Entity				
Filing Fees for Utility under 35 USC 111(a)				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Utility Appl Issue Fee	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:	26025179
Application Number:	14865805
International Application Number:	
Confirmation Number:	1076
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-10103/57
Receipt Date:	10-JUN-2016
Filing Date:	25-SEP-2015
Time Stamp:	09:28:43
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	\$ 480
RAM confirmation Number	061016INTEFSW09293500
Deposit Account	5335
Authorized User	Ann Andrusiak

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)	TIA10103.PDF	39845	no	1
			a31ac0ce0f0c42fc2a9b021a1aeeaa28c6d9111d		
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30594	no	2
			27f587fdb6a0eee6997c8e5d978dfa7fc10286a		
Warnings:					
Information:					
Total Files Size (in bytes):			70439		
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.					



UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/865,805	09/25/2015	David Ofer	TIA-10103/57	1076

25006 7590 05/05/2016
DINSMORE & SHOHL LLP
PO BOX 7021
TROY, MI 48007-7021

EXAMINER

GODENSCHWAGER, PETER F

ART UNIT	PAPER NUMBER
----------	--------------

1767

NOTIFICATION DATE	DELIVERY MODE
-------------------	---------------

05/05/2016

ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

docket@patlaw.com

Supplemental Notice of Allowability	Application No. 14/865,805	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 IDS filed April 26, 2016.
☐ 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 1-17. 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>4/25/2016</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

Issue Classification 	Application/Control No. 14865805	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	I	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
C01G		53	/	66	I	2013-01-01
H01M		2004	/	028	A	2013-01-01

CPC Combination Sets				
Symbol	Type	Set	Ranking	Version

NONE		Total Claims Allowed:	
		17	
(Assistant Examiner)	(Date)	O.G. Print Claim(s)	O.G. Print Figure
/PETER F GODENSCHWAGER/ Primary Examiner.Art Unit 1767	04/27/2016	1	1
(Primary Examiner)	(Date)		

Issue Classification 	Application/Control No. 14865805	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	10	17												
2	2														
3	3														
4	4														
5	5														
6	6														
7	7														
8	8														
9	9														
11	10														
12	11														
13	12														
14	13														
15	14														
16	15														
17	16														

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	17	
/PETER F GODENSCHWAGER/ Primary Examiner.Art Unit 1767	04/27/2016	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

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.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /PFG/

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.

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>				Complete if Known	
				Application Number	14/865,805-Conf. #1076
				Filing Date	September 25, 2015
				First Named Inventor	David Ofer
				Art Unit	1767
				Examiner Name	P. F. Godenschwager
				Attorney Docket Number	TIA-10103/57
Sheet	2	of	2		

[illegible]

Examiner Signature		Date Considered	
-----------------------	--	--------------------	--

*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.

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

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
1 December 2005 (01.12.2005)

PCT

(10) International Publication Number
WO 2005/114768 A1

(51) International Patent Classification⁷: **H01M 4/48**, 4/58

(21) International Application Number:
PCT/US2005/017548

(22) International Filing Date: 19 May 2005 (19.05.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/850,877 21 May 2004 (21.05.2004) US

(71) Applicant (for all designated States except US): **TIAX LLC** [US/US]; 15 Acorn Park, Cambridge, MA 02140 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ONNERUD, Per, T.** [SE/US]; 449 Salem End Road, Framingham, MA 01702 (US). **SHI, Jay, Jie** [US/US]; 12 Marian Road, Acton, MA 01720 (US). **DALTON-CASTOR, Sharon,**

L. [US/US]; 11 Hersam Street, #3, Stoneham, MA 02180 (US). **LAMPE-ONNERUD, Christina** [SE/US]; 449 Salem End Road, Framingham, MA 01702 (US).

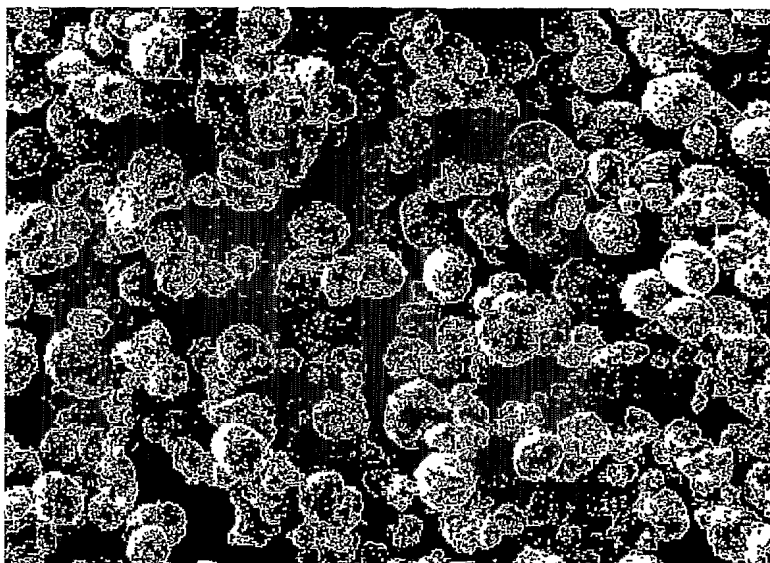
(74) Agent: **DOMINGO, Elias**; Lowrie, Lando & Anastasi, LLP, One Main Street, Cambridge, MA 02142 (US).

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,

[Continued on next page]

(54) Title: LITHIUM METAL OXIDE MATERIALS AND METHODS OF SYNTHESIS AND USE



500X

(57) Abstract: A composition having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$ wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.91 < x + y < 1.3$ can be utilized as cathode materials in electrochemical cells. A composition having a core, having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$ wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.9 < x + y < 1.3$, and a coating on the core, having a formula $\text{Li}_a\text{Co}_b\text{O}_2$ wherein $0.7 < a < 1.3$, and $0.9 < b < 1.2$, can also be utilized as cathode materials in electrochemical cells.



FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO,
SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— *with international search report*

- 1 -

LITHIUM METAL OXIDE MATERIALS
AND
METHODS OF SYNTHESIS AND USE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to lithium metal oxide compositions as well as electrochemical devices utilizing such compositions and, in particular, to lithium-magnesium nickel oxide compositions suitable as components of lithium-ion electrochemical devices.

2. Description of Related Art

Rechargeable lithium and lithium-ion batteries can be used in a variety of applications, such as cellular phones, laptop computers, digital cameras and video cameras, and hybrid electric vehicles etc., due to their high energy density.

Commercially available lithium-ion batteries typically consist of graphite-based anode and LiCoO_2 -based cathode materials. However, LiCoO_2 -based cathode materials can be expensive and typically have relatively low capacity, approximately 150 mAh/g.

Alternatives to LiCoO_2 -based cathode materials include LiNiO_2 -based cathode materials, which can be less expensive. Typical LiNiO_2 -based cathode materials can include compositions having a formula $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ or $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. These materials are relatively more expensive than cobalt-free LiNiO_2 -based cathode material because of the relatively higher cost of cobalt relative to nickel. Furthermore, LiNiCoO_2 -based cathode materials usually have lower safety, cyclability, and first cycle efficiency over LiCoO_2 -based cathode materials because of the lower structural stability and higher surface reactivity of LiNiO_2 type cathodes.

$\text{Li}(\text{Ni}, \text{Co})\text{O}_2$ -based cathode materials have also been disclosed. For example, Lecerf et al., in U.S. Patent No. 4,980,080, disclosed a process of making a cathode material for a secondary battery having a formula $\text{Li}_y\text{Ni}_{2-y}\text{O}_2$ or $\text{Li}_{1-x}\text{Co}_x\text{O}_2$. Xie et al., in U.S. Patent No. 5,750,288, disclosed modified lithium nickel oxide compounds for electrochemical cathodes and cells based on $\text{Li}_x\text{M}_y\text{O}_z$ materials, where M is a non-transition metal selected from the group consisting of aluminum, gallium, tin and zinc. Mayer, in U.S. Patent No. 5,783,333, disclosed a $\text{Li}_x\text{Ni}_y\text{Co}_z\text{M}_n\text{O}_2$ material. Mayer also disclosed, in U.S. Patent Nos. 6,007,947 and 6,379,842, cathode materials having a formula $\text{Li}_x\text{Ni}_y\text{Co}_z\text{M}_n\text{O}_2$ or

- 2 -

Li_xMn_{2-r}M₁O₄ where M is a metal selected from the group consisting of aluminum, titanium, tungsten, chromium, molybdenum, magnesium, tantalum, silicon, and combinations thereof and M₁ is one of chromium, titanium, tungsten, nickel, cobalt, iron, tin, zinc, zirconium, silicon, or a combination thereof. Kumta et al., in U.S. Patent No. 6,017,654, disclosed cathode materials having a formula Li_{1+x}Ni_{1-y}M_yN_xO_{2(1+x)} and LiNi_{1-y}M_yN_xO_p where M is a transition metal selected from the group consisting of titanium, vanadium, chromium, manganese, iron, cobalt, and aluminum and N is a Group II element selected from the group consisting of magnesium, calcium, strontium, barium, and zinc. Sunagawa et al., in U.S. Patent No. 6,040,090, disclosed a positive electrode material based on Li-Ni-Co-Mn-O₂. Peres et al., in U.S. Patent No. 6,274,272, disclosed an active cathode material having a formula Li_LNi_(1-C-A-M)Co_CAl_AMg_MO₂. Gao et al., in U.S. Patent No. 6,277,521, disclosed a lithium metal oxide material containing multiple dopants with a formula LiNi_{1-x}Co_yM_aM'_bO₂ where M is a metal selected from the group consisting of titanium, zirconium, and combinations thereof and M' is a metal selected from the group consisting of magnesium, calcium, strontium, barium, and combinations thereof. Mao et al., in U.S. Patent No. 6,071,649, disclosed LiCoO₂-coated LiNiO₂ or Li(Ni,Co)O₂ materials. None of these disclosed Li-Mg-Ni-O₂-based cathode materials.

Matsubara et al, in U.S. Patent No. 6,045,771, disclosed a cathode material having a formula Li_{y-x1}Ni_{1-x2}M_xO₂, where M is a metal selected from the group consisting of aluminum, iron, cobalt, manganese, and magnesium, $x = x_1 + x_2$, $0 < x_1 \leq 0.2$, $0 < x_2 \leq 0.5$, $0 < x \leq 0.5$, and $0.9 \leq y \leq 1.3$.

Multiple companies are also commercially fabricating cathodes utilizing materials with a general formula LiNiCoMO₂. TODA (earlier Fuji Chemical) manufactures products CA5, CA1505N, and NCA. Honjo-FMC and Nichia (both of Japan) also provide nickel-cobalt-based cathodes. These products typically suffer from low safety properties, and relatively low rate capability.

BRIEF SUMMARY OF THE INVENTION

In accordance with one or more embodiments, the present invention relates to Li_xMg_yNiO₂ materials, which, when utilized in electrochemical applications or systems, can be characterized as being or providing systems that utilize safer, low-cost cathode materials with high capacity, long cycle life, high rate, especially high powerability, as well as high

- 3 -

voltage. In some embodiments, the cathode materials of the present invention can be characterized as being lower cost, having improved chemical stability, and higher operating voltage while providing greater capacity especially, for example, relative to LiCoO_2 - and/or LiNiO_2 - based cathode materials.

5 In accordance with one or more embodiments, the present invention provides a composition having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$ wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.91 < x + y < 1.3$.

In accordance with further embodiments, the present invention provides a composition comprising a core having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$, wherein $0.9 < x < 1.3$,
10 $0.01 < y < 0.1$, and $0.9 < x + y < 1.3$, and a coating on the core having a formula $\text{Li}_a\text{Co}_b\text{O}_2$, wherein $0.7 < a < 1.3$, and $0.9 < b < 1.2$.

In accordance with one or more embodiments, the present invention provides an electrochemical cell comprising a cathode comprising a composition having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$, wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.9 < x + y < 1.3$.

15 In accordance with one or more embodiments, the present invention provides an electrochemical cell comprising a cathode comprising particles consisting of a core having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$, wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.91 < x + y < 1.3$, and a coating on the core. The coating can have a formula $\text{Li}_a\text{Co}_b\text{O}_2$, wherein $0.7 < a < 1.3$, and $0.9 < b < 1.2$.

20 A method of preparing a composition comprising providing a mixture of compounds comprising a lithium source, a magnesium source, and a nickel source and reacting the mixture in an oxidizing atmosphere at a temperature and for a period sufficient to crystallize the mixture into a $\text{Li}_x\text{Mg}_y\text{NiO}_2$ composition wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.91 < x + y < 1.3$.

25 In accordance with one or more embodiments, the present invention provides a method of preparing coated particles. The method can comprise steps of providing a first mixture of compounds comprising lithium, magnesium, and nickel and sintering the first mixture in an oxidizing atmosphere at a first temperature and for a first period sufficient to crystallize the first mixture into core particles having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$, wherein
30 $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.91 < x + y < 1.3$; and coating the core particles with a second mixture comprising compounds comprising lithium and cobalt and sintering the coated core particles at a second temperature and for a second period sufficient to crystallize the coating having a formula $\text{Li}_a\text{Co}_b\text{O}_2$ wherein $0.7 < a < 1.3$, and $0.9 < b < 1.2$.

- 4 -

In accordance with one or more embodiments, the present invention provides a particle comprising a core material having a composition of a formula $\text{Li}_{1-y}\text{Mg}_y\text{NiO}_2$ where Mg and Li are predominantly in a crystallographic 3a site and Ni is predominantly in a crystallographic 3b site and $0.01 < y < 0.1$.

Other advantages, novel features, and objects of the invention should become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings, which are schematic and not intended to be drawn to scale.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred, non-limiting embodiments of the present invention will be described by way of example with reference to the following, accompanying drawings. In the drawings, each identical or nearly identical component that is illustrated in various figures is typically represented by a like numeral. For clarity, not every component may be labeled in every drawing nor is every component shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the drawings:

FIG. 1 is a copy of photomicrograph, representing a typical lithium-magnesium-nickel oxide composition in accordance with one or more embodiments of the present invention; here represented by spherical $\text{LiMg}_{0.025}\text{NiO}_2$;

FIG. 2 is an X-ray diffraction pattern of the composition shown in FIG. 1;

FIG. 3 is a graph showing the discharge profile, at different discharge rates, of the material shown in FIG. 1;

FIG. 4 is a copy of photomicrograph of a typical lithium-cobalt oxide-gradient coated lithium-magnesium-nickel oxide composition in accordance with one or more embodiments of the present invention; here represented by an about 5 mol% $\text{LiCoO}_2\text{:LiMg}_{0.025}\text{NiO}_2$;

FIG. 5 is an XRD graph of the coated composition shown in FIG. 4;

FIG. 6 is a graph showing the discharge profile of the composition shown in FIG. 4 having about a 5 mol % coating level at various rates;

FIG. 7 is a graph showing the discharge profile of the composition shown in FIG. 4 having about a 10 mol % coating level at various rates;

FIG. 8 is a graph showing the discharge profile of the composition shown in FIG. 4 having about a 15 mol % coating level at various rates;

- 5 -

FIG. 9 is a graph showing the area specific impedance for a $\text{LiMg}_{0.025}\text{NiO}_2$ composition with about a 5 mol % LiCoO_2 gradient coating, using about a 1s and an 18s pulse according to protocol 3, in accordance with one or more embodiments of the invention;

FIG. 10 is a graph showing the area specific impedance for various $\text{LiMg}_{0.025}\text{NiO}_2$ compositions, using 1s and 18s pulses according to protocol 3, in accordance with one or more embodiments of the invention;

FIG. 11 is a graph showing the X-ray diffraction patterns showing peak profiles at about 5 mol %, 10 mol %, and 15 mol % gradient coating levels of a LiCoO_2 composition (with an enlarged portion shown in the right side), in accordance with one or more embodiments of the invention;

FIG. 12 is a graph showing the capacity retention of cells during about a 1 C discharge cycling utilizing a) LiNiO_2 , b) LiMgNiO_2 , c) about 5 mol % LiCoO_2 coated $\text{LiMg}_{0.025}\text{NiO}_2$, and d) CA1505N(TODA Co., Japan); and

FIG. 13 is a graph showing the differential scanning calorimetry profile of a) $\text{LiMg}_{0.025}\text{NiO}_2$, b) about 5 mol % LiCoO_2 coated $\text{LiMg}_{0.025}\text{NiO}_2$, and c) TODA NCA-02 electrodes, which have been subjected to about 4.2V charging (100% state-of-charge) and immersed in electrolyte.

DETAILED DESCRIPTION OF THE INVENTION

This invention is not limited in its application to the details of construction and the arrangement of components or compounds set forth in the following description, including the various examples, or illustrated in the drawings. The invention is capable of other embodiments and of being practiced or of being carried out in various ways. Also, the phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. The use of “including,” “comprising,” or “having,” “containing,” “involving,” and variations thereof herein, is meant to encompass the items listed thereafter and equivalents thereof as well as additional items.

In accordance with one or more embodiments, the present invention provides one or more compositions and one or more methods for forming the various compositions. The compositions can be used as a cathode active material in, for example, rechargeable lithium and lithium-ion electrochemical devices, such as but not limited to, batteries. In accordance with one or more embodiments, the present invention can also provide rechargeable lithium

- 6 -

batteries or lithium-ion batteries, as well as methods of preparation and use, utilizing, for example, the compositions of the invention. The electrochemical cells utilizing the compositions of the present invention can be characterized as, inter alia, being low cost and chemically stable while providing high capacity during a long operating life.

5 In accordance with some embodiments, the composition of the present invention typically exhibits improved capacity, cyclability, and safety over LiCoO_2 and LiNiO_2 materials when such materials are utilized in electrochemical devices, including, but not limited to primary and secondary batteries. The materials of the present invention can provide economic advantages because they are typically less expensive to produce and/or
10 utilize compared to LiCoO_2 , LiNiO_2 or $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -based materials.

In accordance with one or more embodiments, the present invention provides a lithium metal oxide composition having a first metal substantially associated with an a-site and a second metal substantially associated with a b-site in a crystalline lattice. The a-site can be crystallographically referred to as the 3a site and the b-site can be referred to as the 3b
15 site in a $R\bar{3}m$ crystal lattice. In accordance with some embodiments of the invention, the first metal can be associated at the 3a site along with, for example, lithium, and the second metal can be associated at the 3b site. Preferably, the first metal or, in some cases the second metal, can provide crystalline stability during lithium intercalation and de-intercalation processes when, for example, the materials or compositions of the present invention are utilized as
20 components of electrochemical devices. By providing such a structure, the composition of the present invention can be advantageously utilized as a cathode in electrochemical devices because, it is believed, the first metal can stabilize, at least partially, the crystal lattice during lithium intercalation and de-intercalation processes.

In accordance with one or more preferred embodiments of the invention, the
25 composition can comprise a lithium-magnesium-nickel oxide wherein lithium and magnesium are crystallographically associated with the 3a site and nickel is crystallographically associated with the 3b site.

In accordance with one or more embodiments, the present invention provides a composition having a general formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$, where $0.9 < x < 1.3$, and $0.01 < y < 0.1$,
30 $0.91 < x + y < 1.3$, preferably, $0.9 < x < 1.1$ and $0.02 < y < 0.05$. The crystalline characteristics of the composition can be characterized as having lithium and magnesium associated with the 3a site and the nickel as being associated with the 3b site.

- 7 -

In accordance with further embodiments, the present invention provides a particle comprising a core or interior layer having one or more layers of a metal oxide coating applied thereon. The coating layer can comprise a second lithium intercalating material including, for example, a compound having a formula $\text{Li}_a\text{Co}_b\text{O}_2$, where $0.7 < a < 1.3$, and $0.9 < b < 1.2$. In some cases, the coating layer can be characterized as having a Co/Ni molar ratio that ranges from about 0.01 to about 1.4, relative to the amount of nickel in the core layer. In still further embodiments of the invention, $0.9 < a < 1.3$, $1.8 < b < 2.2$ and the Co/Ni molar ratio can range from about 0.02 to about 0.8. The one or more layers can be characterized as having a concentration gradient with respect to the amount of cobalt relative to distance, e.g. radial distance, from the surface of the particle. The nature of the concentration gradient of the amount cobalt, relative to distance from the surface, can range from about 100 %, substantially all cobalt and none or only negligible trace amounts of nickel, at the outer surface of the particle to about 0 %, substantially none or only negligible trace amounts of cobalt at the coating/core interface. The nature or shape of the gradient profile can vary. For example, the gradient profile can linearly decrease relative to radial distance from the surface.

In accordance with still further embodiments, the invention can be characterized as providing a particle comprising a lithium magnesium nickel oxide core having a lithium cobalt oxide coating layer. The amount of the coating layer can range from about 0.01 wt % to about 30 wt% of the particle.

The present invention further provides one or more synthesis techniques that provides a first metal having a preferential association with the 3a site and, in some cases, provides a second metal having a preferential association with the 3b site. In accordance with still other embodiments, the present invention provides synthesis techniques that can decrease any tendency by the second metal to associate with the 3a site.

The first metal can provide crystalline stability to the lithium mixed metal oxide material during lithium intercalation/de-intercalation cycling processes. Thus, the techniques of the present invention can provide a chemically stable material that may be suitable as components, e.g. cathodes, in electrochemical devices and be characterized as having high capacity, low cost as well as high voltage and high rate with improved cycle life.

In accordance with one or more embodiments, the techniques of the present invention can utilize precursor compounds that can form a lithium metal oxide, preferably a lithium metal oxide doped with a crystal lattice stabilizing metal. In accordance with other embodiments, the techniques of the present invention can provide or promote processing

- 8 -

conditions that favor the formation of ionic species from precursor compounds that can preferentially become associated with specific crystallographic sites. The processing conditions of the present invention can promote formation of metal oxide species as well as association of such species with a particular, predetermined crystallographic site. For example, the techniques of the present invention can utilize one or more lithium donor compounds, one or more metal donor compounds that preferentially can become associated with a 3a crystallographic site, and in some cases, one or more metal donor compounds that preferentially become associated with a 3b crystallographic site. Thus, in accordance with one or more embodiments, the present invention can utilize a lithium donor compound, a magnesium metal donor compound, and a nickel metal donor compound; the processing conditions can promote ionic species formation, intermingling, and crystallization to form a lithium mixed metal oxide wherein a first metal can be preferentially associated with a 3a crystallographic site and a second metal can be preferentially associated with a 3b site.

In accordance with further embodiments, the techniques of the present invention can provide a lithium magnesium nickel oxide composition. For example, one or more techniques can utilize precursor compounds including, for example, those selected from the group consisting of a lithium donor, a magnesium donor, and a nickel donor. In some cases, one or more oxidizing agents or compounds can also be utilized. Thus, the precursor compound mixture can comprise, for example, a lithium source, an oxidizing agent, a first metal donor, and a second metal donor. The lithium source, the oxidizing agent, the first metal donor, and the second metal donor, preferably, can undertake one or more phase changes or phase transitions at about the same processing conditions, e.g. at about the same processing temperature range. Preferably, the elements of the selected precursor compounds can maintain their respective predetermined valences until, or in some cases through, the phase change. Likewise, the processing conditions utilized inhibit or at least do not promote any valance changes. Thus, in accordance with one or more preferred embodiments of the present invention, the precursor compounds, or oxides of the respective donor components, can be subject to processing conditions that promote or maintain chemical stability until reaction to a desired phase.

The lithium donor or source can comprise lithium hydroxide, lithium carbonate, or mixtures thereof. The oxidizing agent can comprise lithium nitrate or nickel nitrate or mixture thereof. In some cases, the lithium source can comprise or consist of lithium nitrate as well as lithium hydroxide. The first metal donor can comprise magnesium hydroxide,

- 9 -

magnesium carbonate, magnesium oxide, or mixtures thereof. The second metal donor can comprise nickel hydroxide, nickel sulfate, nickel nitrate, nickel oxide, or mixtures thereof.

The precursor compounds can have any form that facilitates mixing into the precursor mixture. For example, the precursor mixture can comprise a powder mixture of each of the precursor compounds or a slurry of each of the precursor compounds. Moreover, the precursor compound can be a masterbatch comprising hydroxides of lithium, the first metal donor, and/or the second metal donor. The oxidizing agent can be incorporated into the masterbatch as desired to facilitate processing and storage before utilization. In accordance with one or more embodiments, the precursor compounds can have desired a structure that, preferably, promotes efficient utilization of the lithium metal oxide materials of the present invention. Thus, the synthesis techniques of the invention can provide morphologically desirable lithium metal oxide materials.

The precursor compounds can have a variety of shapes that can be transformed to a material that can coat or be coated to form a component of an electrochemical device. For example, one or more of the precursor powder compounds can be spherically-shaped. Other shapes can be utilized as desired to accommodate or suit an end-user preference. Preferably, the synthesis process of the present invention can maintain, at least partially, the spherical shape throughout the processing or synthesis steps to provide, for example, a lithium magnesium nickel oxide material suitable as a cathode electrode in, for example, rechargeable electrochemical devices. Thus, in accordance with one or more preferred embodiments, the precursor mixture comprises a nickel donor, such as but not limited to nickel hydroxide, having a spherical shape. However, any shape and form of the starting materials of the composition of the present invention can be utilized.

In accordance with still further embodiments, the nickel donor can comprise a high density, e.g. high tap density, nickel hydroxide.

The $\text{Li}_x\text{Mg}_y\text{NiO}_2$ compositions of the present invention can be prepared by utilizing precursor compounds with pre-defined or pre-selected particle sizes and morphologies. Any particle size can be utilized to create the composition of the present invention. For example, the particle size of a nickel donor precursor such as $\text{Ni}(\text{OH})_2$ can be in the range of about 2 μm to about 20 μm .

In accordance with one or more embodiments, the material molar ratios of the precursor compounds can be selected to provide a composition having the general material formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$, where $0.1 < x < 1.3$, and $0.01 < y < 0.1$, $0.9 < x + y < 1.3$. In some

- 10 -

cases, the ratios can be selected so that $0.9 < x < 1.1$, and $0.02 < y < 0.05$. In still other cases, x can be about $1-y$.

In yet other embodiments in accordance with the present invention, the $\text{Li}_x\text{Mg}_y\text{NiO}_2$ or $\text{Li}_{1-y}\text{Mg}_y\text{NiO}_2$ materials can have any one of the following formula: $\text{Li}_{1.05}\text{Mg}_{0.005}\text{NiO}_2$,
5 $\text{Li}_{1.05}\text{Mg}_{0.01}\text{NiO}_2$, $\text{Li}_{1.05}\text{Mg}_{0.02}\text{NiO}_2$, $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$, $\text{Li}_{1.05}\text{Mg}_{0.030}\text{NiO}_2$, $\text{Li}_{1.05}\text{Mg}_{0.04}\text{NiO}_2$,
and $\text{Li}_{1.05}\text{Mg}_{0.05}\text{NiO}_2$. Thus, the precursor compounds can be selected in such ratios that provide such compositions.

The precursor compounds are typically pre-mixed to allow homogeneous mixing. In still further embodiments, the materials of the present invention can be crystallized by, for
10 example, heating to sinter and facilitate crystallization into the compositions of the present invention.

The synthesis process can comprise mixing the precursor compounds into a substantially homogeneous mixture. The synthesis process can further comprise heating the precursor mixture in one or more heating stages or steps, e.g. two or more heat soaks,
15 according to a predetermined heating profile. The synthesis process typically promotes oxidation, or oxyhydroxide formation, of the corresponding donor components; mixing, typically ionic mixing, of such components; and crystallization into a lithium metal oxide composition, wherein the first metal of the composition, e.g. magnesium, is associated with a
3a site and the second metal, e.g. nickel, is associated with the 3b site. For example, in a
20 lithium-magnesium-nickel oxide composition, the mixture can be heated to a first heating temperature that promotes preferential formation of Ni^{3+} over Ni^{2+} .

In accordance with one or more embodiments of the invention, the first heating step or stage can involve heating the green, precursor mixture to allow oxide formation and/or ion mixing without, or at least minimal, valence changes of the donor compounds. For example,
25 the precursor mixture can be heated to a heat soak temperature of about 450°C in a first heating step. This first heat soaking temperature can range from about 350°C to about 700°C . The second heating step can comprise heating to promote crystallization of the transformed oxide mixture by, for example, heat soaking at a second heat soak temperature of about 700°C . The second heat soaking temperature can range from about 600°C to about
30 800°C .

Preferably, the first soaking temperature is maintained until the precursor compounds have been substantially transformed into their oxide counterparts. For example, the first soaking temperature can be maintained for about one hour but can be maintained for as long

- 11 -

as about six hours. In accordance with other embodiments, the first heat soak condition can be maintained for any duration such that the synthesis procedure can proceed to the next heating stage to commence or promote crystallization, i.e., without maintaining a first soaking temperature. The second soaking temperature can be maintained, for example, until
5 the lithium metal oxide has crystallized to a desired extent. Thus, for example, the second heat soak can be maintained for about one hour but can be maintained for as long as about six hours.

Heating, as well heat soaking, can be performed with exposure to an oxidizing atmosphere such as air or pure oxygen.

10 The first heating step can comprise raising the temperature at a rate sufficient to promote oxide formation while reducing any tendency to destabilize the precursor morphology. For example, the precursor mixture can be heated at a rate of about 20° C per minute, about 10° C per minute, or even about 5° C per minute. Control of the heating rate may depend on several factors including, but not limited to, the amount being processed, the
15 desired relative composition, as well as the effective area exposed to the oxidizing atmosphere. The second heating stage can comprise raising the temperature sufficient to facilitate crystallization such that the first metal tends to be associated with the 3a site and the second metal tends to be associated with the 3b site. For example, the oxide mixture can be heated at a rate of about 10° C per minute, about 5° C per minute, or even about 2° C per
20 minute.

After heat treatment, the materials can be allowed to cool naturally to room temperature by, for example, natural convection. Heat and soaking can be performed in any suitable equipment. For example, a furnace or oven accommodating the mixture can be utilized. The furnace can be supplied with air and/or oxygen.

25 The sintered, crystallized material can be ground in any suitable grinding apparatus. For example, a mortar grinder (e.g., Model RM100 grinder available from Retsch/Brinkmann or Brinkmann Instruments, Inc., Westbury, New York) fitted with an agate mortar and pestle, can be utilized to grind the crystallized composition to render it with a desired particle size. Other suitable grinding methods or systems can include, for example, ball milling, jet milling,
30 attritor mill, hammer mill and pin mill. The desired particle size can vary and can depend on the specific application or use. Thus, in accordance with one or more embodiments of the invention, the $\text{Li}_x\text{Mg}_y\text{NiO}_2$ composition can be formed as particles by grinding for about five

- 12 -

minutes until a mean particle size of about 2 μm to about 20 μm , preferably about 5 μm to about 10 μm , is achieved.

In accordance with one or more preferred embodiments of the present invention, the $\text{Li}_x\text{Mg}_y\text{NiO}_2$ composition, typically as particles, can further comprise a coating layer that further improves a first cycle efficiency, life, and/or safety or even reduces gassing when the composition is utilized as a cathodic material in electrochemical devices. In accordance with still further embodiments of the invention, the $\text{Li}_x\text{Mg}_y\text{NiO}_2$ particles further comprise one or more coating layers that reduces any gelling tendencies when the particles are prepared as an electrode paste. For example, the particles can be coated to reduce the likelihood of gelling in a mixture comprising NMP, PVDF, $\text{Li}_x\text{Mg}_y\text{NiO}_2$, and conductive carbon, which is yet another advantage over non-coated nickelates.

In accordance with one or more embodiments of the invention, the coating layer can comprise a composition having a formula LiCoO_2 . The coated $\text{Li}_x\text{Mg}_y\text{NiO}_2$ particles can be prepared by mixing therewith a lithium salt solution or mixture such as, but not limited to LiNO_3 , LiOH , LiAc , Li_2SO_4 , Li_2CO_3 , with a cobalt containing salt solution. In accordance with one or more embodiments of the invention, the lithium salt can comprise LiNO_3 and the cobalt salt can comprise $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The molar ratio of Li/Co can vary but typically ranges from about 0.6 to about 1.4. Preferably, the Li/Co molar ratio ranges from about 0.95 to about 1.05 so that the molar ratio of the Co content, in the coating layer, to the Ni content, in the core layer, ranges from about 0.01 to about 0.4, more preferably from about 0.05 to about 0.15.

If any water, which is typically carried with the salts, is present, it is preferably allowed to evaporate utilizing any suitable techniques. For example, mixture can be heated on a hot plate with stirring until dry, or in a rotating drying oven.

The precursor-coated material can then be heated or sintered in air using any suitable apparatus, such as a muffle furnace to facilitate oxidation and/or crystallization of the coating layer on the core. For example, the coating layer can be synthesized by raising the temperature of the precursor coated $\text{Li}_x\text{Mg}_y\text{NiO}_2$ particles at any suitable rate, such as about 5° C per minute, and maintained or soaked at a temperature of about 450° C for about one hour. A second soaking temperature can be utilized by raising the temperature at a rate of about 2° C per minute and maintained at a temperature of about 700° C for about two hours to promote crystallization of the coating layer. Such an exemplary sintering treatment can provide a coated material having a concentration gradient structure wherein more cobalt can

- 13 -

be present at or near the outer surface compared to the region at or near the core layer. Other techniques may be utilized that provides a coated core material having the composition of the present invention.

5 The drying stage can be performed until the mixture is sufficiently dry. For example, drying can be performed by heating at a rate of about 2° C per minute to a temperature of about 110° C. The drying temperature can be maintained as long as necessary and may last from 0 minutes to one or more hours.

10 The first heating rate to produce the one or more coating layers can vary and may range from about 2° C per minute to about 10° C per minute. The first heat soaking temperature can range from about 300° C to about 500° C. This first heat soaking temperature can be maintained until the sufficient or desired oxide conversion has been achieved. It can be maintained from 0 minutes to one or more hours. The second heating rate can vary from about 2° C per minute to about 10° C per minute. The second heat soaking temperature can range from about 650° C to about 750° C. It is believed that higher
15 soaking temperatures may promote degradation of the core layer to other than the preferred crystallographic arrangement. The coated particles can be allowed to cool to room temperature.

Any suitable equipment may be utilized in the drying/heating/soaking process including, for example, any oven or furnace that provides an appropriate oxidizing
20 atmosphere.

The sintered, coated material can be further processed to obtain a particle sized between about 8 μm to about 12 μm . For example, the sintered, coated material can be ground for about five minutes in a mortar grinder fitted with an agate mortar and pestle.

25 Examples

The function and advantages of these and other embodiments of the present invention can be more fully understood from the examples below. The following examples illustrate the benefits and/or advantages of the compositions and techniques of the present invention but do not exemplify the full scope of the invention.

30 In the examples, the following test protocols were performed.

- 14 -

Protocol 1. Rate capability test and formation -1st cycle efficiency

A coin cell was used for material life test utilizing lithium metal as the counter electrode. The positive electrode of the coin cell was made from a composite cathode prepared in accordance with Example 2. The electrolyte was EC/DEC (1:1)-LiPF₆, 1 M (available from EM Industries, Inc., Hawthorne, New York) and the separator was a glass fiber material (available from Fisher Scientific).

The cell was fully charged and discharged at a rate of C/20 for first cycle efficiency measurements, which is the ratio of the discharge capacity vs the charge capacity. Thereafter the cell was cycled at rates of about C/5, C/2, 1C, 2C, 3C, and 5C from about 2.7 volts to about 4.2 volts. 1C rate was defined as about 150mAh/g discharge in 1 hour.

Protocol 2. Life cycle test.

A coin cell was used for material life test. The positive electrode of the coin cell was made from a composite cathode, and the negative was made from a composite anode, consisting of graphite as mesophase carbon microbeads (MCMB 2528, 90 wt%), PVDF binder (7 wt%) and carbon black (3 wt%). The electrolyte was EC/DEC (1:1)-LiPF₆, 1 M (available from EM Industries, Inc., Hawthorne, New York) and the separator was a glass fiber material (available from Fisher Scientific).

The cell was initially fully charged and discharged for 3 cycles at about C/5 rate, deep cycle. The deep cycles consisted of charging to about 4.2 V (fully charged) and discharging to about 2.7 V (fully discharged). The cell was fully charged, to about 4.2 V (100 % state-of-charge (SOC)), cell was then discharged to about 20 % of full capacity at about 1C rate current to reach about an 80 % SOC. Then the cell was cycled discharging about 10% (to about 70 % SOC) and charged 10% (to about 80 % SOC) at about 1C rate current, typically referred to as a shallow cycle.

A deep cycle was performed after every 200 shallow cycles. This test provided an indication of the effective life of the cell under evaluation.

Protocol 3. Area Specific Impedance (ASI) Measurement.

The ASI, in Ωcm^2 , at various starting SOC conditions was determined by pulse discharging a coin cell. ASI was calculated according to:

- 15 -

$$ASI = A \cdot (\Delta V / I),$$

where A is the electrode area in cm^2 , where I is the discharge current pulse at a rate of about 6C. The voltage variation (ΔV) is the voltage change during the discharge pulse.

For example, at a SOC = 90 %, the initial voltage is measured. The cell is discharged
5 at a rate of 6C and the final voltage is measured after 18 sec.

ASI can correlate to the potential available power and allows for a comparison of power capability between materials and formulations for Li-ion cells. This can be particularly important for high pulse power applications.

10 Example 1. Synthesis of $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ Composition.

A $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ composition was prepared and evaluated. The composition was prepared by dry mixing:

about 242.91 g $\text{Li}(\text{OH})_2$ (anhydrous fine powder available from Sigma-Aldrich, Inc., St. Louis, Missouri)

15 about 14.79 g $\text{Mg}(\text{OH})_2$ (fine powder available from Alfa Aesar, Ward Hill, Massachusetts)

about 34.97g LiNO_3 (crystals available from Alfa Aesar, Ward Hill, Massachusetts)

The mixed materials were added to about 940.31 g $\text{Ni}(\text{OH})_2$ (#543 high density spherical powder available from OM Group, Inc., Cleveland, Ohio) in a 1 liter jar. The
20 compounds were mixed by shaking in the jar.

The homogeneous precursor powders (precursor compounds) were placed in alumina crucibles and sintered.

Sintering was performed by heating at a rate of about $5^\circ \text{C}/\text{minute}$ to about 450°C and held at about 450°C for about four hours. The temperature was then raised at about
25 $2^\circ \text{C}/\text{minute}$ to about 700°C and held for about four 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. The powder material was sieved through a No. 270 mesh to remove larger particles and to ensure a desired $10 \mu\text{m}$ particle size.

30 FIG. 1 is a copy of scanning electron micrograph showing the morphology of the about $10 \mu\text{m}$ spherical core material. An X-ray diffraction pattern (XRD) analysis was performed and showed that the produced composition was phase-pure with no visible

- 16 -

impurities. FIG. 2 is a copy of the XRD plot of the resultant composition. The XRD data shows that the resulting powder is essentially free of impurities.

Example 2. Fabrication and Electrochemical Performance Evaluation of $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ -based Electrochemical Cells.

A $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ cathode was fabricated by mixing about 90 wt% active cathode material powder produced as described in Example 1, about 6 wt% carbon black (AB100% available from Chevron Phillips Chemical Company LP, The Woodlands, Texas), and about 4 wt% K1120 binder containing 12% PVDF in NMP (available from Kureha Chemical of Japan). Additional NMP (n-methyl pyrrolidone) was added to produce a desired viscosity and promote mixing.

The solution was mixed in a 250 ml jar with about 50 steel balls on a paint shaker for about 30 minutes. The mixed slurry was coated onto an aluminum foil, about 20 μm thick, with a doctor blade having about a 100 μm micron coating gap.

The coated foil was dried at about 130° C for about thirty minutes. The dried, coated foil was then densified by passing the dried, coated foil through pressurized calender rolls, about 3 inch diameter, set at about 100 psi. The densified, dried, coated foil was cut into about 2 cm^2 disks for use as electrodes. The active material weight on the disk electrodes was typically about 20 mg. The disk electrode was dried at about 80° C under vacuum for about sixteen hours before cell assembly.

A coin cell (Hosen type #2025) was assembled by utilizing the disk electrode as the cathode. The coin cell was comprised of a glass fiber separator containing EC/DEC (1:1)- LiPF_6 , 1 M electrolyte (available from EM Industries, Inc., Hawthorne, New York) and a lithium metal anode. All assembly operations were performed in an argon-filled glove box wherein water and oxygen levels were less than about 2 ppm.

The assembled coin cell was evaluated using a cycler/tester (available from Maccor, Inc., Tulsa, Oklahoma) for capacity, efficiency, rate capability, power and cyclability, according to protocols 1, 2, and 3, described above. The electrochemical performance of the $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ composition (i.e., 0 % coating) data are listed in Table 1 below. The discharge voltage profiles at different discharge rates are shown in FIG. 3, which shows that the capacity of the $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ composition was typically about 190 mAh/g.

Table 1. Electrochemical performance of $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ -based cell.

$\text{LiMg}_y\text{NiO}_2$ Core with LiCoO_2 Coating Level mol %	Specific Capacity at Specified Rate					
	1 st Cycle Efficiency %	C/5 mAh/g	1C mAh/g	2C mAh/g	3C mAh/g	5C mAh/g
0%	87	203	192	185	180	172
5%	92	202	194	186	181	165
10%	89	197	190	179	175	162
15%	90	191	184	173	169	141

Example 3. Safety Testing of $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ Cathode.

5 Coated cathodes prepared and evaluated. The densified electrode prepared as described in Example 2 was cut into flag-shaped electrodes of about $60 \times 50 \text{ mm}^2$. The active material weight on the electrode was typically about 300 mg. Similar to the cathode, an anode was prepared with formulation of MCMB:PVDF (93:7) was coated on a copper foil and cut to form $60 \times 50 \text{ mm}^2$ flag electrodes. These were similarly densified by calendaring at 175 psi. The flag electrodes were dried at about 80°C , under vacuum for about sixteen hours.

A two-electrode bag cell was assembled. The cell was comprised of the dried anode and cathodes, separated by a glass fiber separator with a rectangular size of about $65 \times 55 \text{ mm}^2$. About 1.6 ml of EC/DEC (1:1)- LiPF_6 , 1 M electrolyte was allowed to soak into the electrodes and separator and the assembly was compressed between two $70 \times 60 \text{ mm}^2$ glass plates. The whole assembly was put into an aluminum- laminated bag, approximately $80 \times 70 \text{ mm}^2$, and sealed under vacuum.

All assembly operations were performed in an argon-filled glove box wherein water and oxygen levels were less than about 2 ppm.

20 The bag cells were charged and discharged at about C/10 current rate, between about 4.1 V to about 2.7 V, then charged at about C/5 current rate to a capacity of about 180 mAh/g to about 200 mAh/g.

The cells with charged composite cathode were disassembled in an argon-filled glove box. The composite cathode powder was removed from the aluminum current collector. The composite electrode powder, with EC/DEC(1:1)- LiPF_6 , 1 M electrolyte in a weight ratio of

- 18 -

powder/electrolyte of 1:1, was loaded into a sealed pressure tight DSC pan. DSC measurements were performed with a continuous scan rate of about 5° C/minute up to about 450° C.

5 The safety data shown in FIG. 13 shows DSC curves of $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ and 5% LiCoO_2 coated material compared to $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (CA1505N cell available from TODA Co., Japan). The DSC curves provide a signature of chemical reactivity during exothermic reactions.

Example 4. Comparison to $\text{Li}_{1.05}\text{NiO}_2$ -based Electrochemical Cells.

10 A $\text{Li}_{1.05}\text{NiO}_2$ composition was prepared by dry mixing:
about 244.42 g $\text{Li}(\text{OH})_2$ (anhydrous fine powder)
about 35.18 g LiNO_3 (crystals)

The mixed materials were added to about 946.15 g $\text{Ni}(\text{OH})_2$ (OM Group, Inc. #543 High density spherical powder) in a 1 liter jar. The precursor powder mixture was mixed by
15 shaking.

The precursor powders were placed in alumina crucibles and sintered. Sintering was performed by heating at a rate of about 5° C/minute to about 450° C and held at about 450° C for about four hours. The temperature was raised at about 2° C/minute to about 700° C and held for about four hours.

20 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. The powder material was sieved through a No. 270 mesh to remove large particles and to ensure the desired 10 μm particle size. When subjected to XRD analysis, this material was shown to be phase-pure with no visible impurities. Electrochemical measurements of this
25 powder were performed in accordance with the procedure described in Example 2. The performance results are listed in Table 2 (i.e., 0 % coating).

- 19 -

Table 2. Electrochemical performance of LiNiO₂-based cell.

LiNiO ₂ Core with LiCoO ₂ Coating Level atom%	Specific Capacity at Specified Rate					
	1 st Cycle Efficiency %	C/5 mAh/g	1C mAh/g	2C mAh/g	3C mAh/g	5C mAh/g
0%	89	211	192	184	178	154
5%	88	214	203	197	190	166
10%	90	209	196	192	184	168
15%	89	197	185	179	172	151

The data show that the performance, as quantified by specific capacity, of the LiMg_yNiO₂-based electrochemical cells of the present invention (see Table 1) are amongst the highest when comparing to the performance of typical lithium-nickel oxide materials.

Example 5. Comparison to LiCoO₂-based Electrochemical Cells.

A comparable composite cathode in an electrochemical cell was prepared using LiCoO₂ (C-5 grade available from Nippon Chemical Industrial Co., LTD., Tokyo, Japan) as the active material. Similar coin cells were prepared as in the previous example for evaluation.

The electrochemical data of this material are listed in Table 3.

Table 3. Electrochemical performance of LiCoO₂-based cell.

Sample	1 st Cycle Efficiency %	Specific Capacity at Specified Rate				
		C/5 mAh/g	1C mAh/g	2C mAh/g	3C mAh/g	5C mAh/g
LiCoO ₂	97	157	143	127	108	71

The data show that the electrochemical performance of the Li_{1.05}Mg_{0.025}NiO₂-based electrochemical cell of the present invention (see Table 1) exceeds the performance of typical lithium-cobalt oxide-based cells, which is the dominating material in the market presently.

- 20 -

Example 6. Performance of Varying Dopant Levels in $\text{Li}_{1.05}\text{Mg}_y\text{NiO}_2$ Material ($y = 0.005, 0.01, 0.02, 0.025, 0.03, 0.04, \text{ and } 0.05$).

Seven $\text{Li}_{1.05}\text{Mg}_y\text{NiO}_2$ compositions were prepared and evaluated where y varied from 0.005, 0.01, 0.02, 0.03, 0.04 and to 0.05. The synthesis procedure for these compositions were substantially similar to the procedure described in Example 1 except that the levels of $\text{Mg}(\text{OH})_2$ were varied accordingly to obtain the various dopant levels.

When subjected to XRD analyses, all samples except for the sample having $y = 5\%$ were shown to be phase-pure with no visible impurities. For this latter composition, $\text{Li}_{1.05}\text{Mg}_{0.05}\text{NiO}_2$, impurities were detected that indicated the presence of mixed magnesium oxides.

All samples were then tested electrochemically in coin cells prepared similar to the procedure described in Example 2. The results are listed in Table 4.

Table 4. Electrochemical Properties of $\text{LiMg}_y\text{NiO}_2$ at varying Mg doping levels.

Mg Doping Level in $\text{LiMg}_y\text{NiO}_2$	Specific Capacity at Specified Rate						
	1 st Cycle Efficiency %	C/20 mAh/g	C/5 mAh/g	1C mAh/g	2C mAh/g	3C mAh/g	5C mAh/g
0	89	227	211	192	184	178	154
0.005	90	226	210	191	183	176	166
0.01	90	223	207	191	184	178	169
0.02	89	218	204	189	183	178	169
0.025	87	214	203	192	185	180	172
0.03	87	210	199	187	181	176	167

The data in Table 4 show that the electrochemical performance, e.g. at specific capacity at 1C rate, of the $\text{LiMg}_y\text{NiO}_2$ -based cells of the present invention was better when compared to the performance of LiNiO_2 -based cells, and superior to the performance of a LiCoO_2 -based cells.

Example 7. Synthesis of $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ Core Particles Coated with a LiCoO_2 Layer.

In this example, a lithium-magnesium-nickel oxide composition, substantially prepared as described in Example 1, was coated with a lithium-cobalt oxide layer.

To synthesize the coating layer, about 105.55 g LiNO_3 (crystalline powder, available from Alfa Aesar, Ward Hill, Massachusetts) and about 445.50 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (crystalline aggregates, also available from Alfa Aesar) were dissolved in about 200-300 ml distilled

- 21 -

water. To which, about 1000 g of the $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ powder substantially prepared as described in Example 1 was added.

The excess water was removed by evaporation on a hot plate with stirring until the mixture became a thick slurry. The slurry was poured into an alumina crucible and sintered under the following heating profile: heat at a rate of about 2°C/min to about 110°C , hold for about one hour at about 110°C , heat at a rate of 5°C/min to about 450°C , heat soak for about one hour at about 450°C , heat at a rate of about 2°C/min to about 700°C , and heat soak for about two hours at about 700°C .

The prepared sample was allowed to cool naturally to room temperature. Once cooled, it was ground for about five minutes to break up any agglomerates and sieved through a No. 270 mesh screen.

XRD analysis shows that the prepared coated composition had a gradient profile, with no visible impurities, as can be seen in the copy of the XRD plot presented in FIG. 5 represented here by 5 mol % LiCoO_2 coated $\text{LiMg}_{0.025}\text{NiO}_2$. A copy of an SEM photomicrograph for the same sample, FIG. 4, shows that the coated powder composition maintained its spherical, about $10 \mu\text{m}$, morphology.

Table 1 lists rate capability and first cycle efficiency of $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ core materials coated with various levels of LiCoO_2 coating. FIGS. 6-8 are graphs showing the discharge profile of the LiCoO_2 -coated $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ -based core composition having, respectively, about 5 mol% coating, about 10 mol% coating, and about 15 mol% coating. The profiles show that the lithium-magnesium-nickel composition can be coated with up to about 15 mol% lithium-cobalt oxide layer and retain about the same electrochemical performance. FIG. 11 is an XRD comparison of these samples showing increasing gradients with amount LiCoO_2 coating.

Example 8. Evaluation of LiCoO_2 -coated $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ Core Material.

Two gradient coated $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_2$ materials were synthesized and coated with about 10 % and about 15% LiCoO_2 using the method in Examples 1 and 7. The gradient coating was detected by studying the increasing degree of asymmetry in the Bragg reflections. In particular, the peak 104 at about 44.4° in 2-theta was used (FIG. 11) to show how the asymmetry of peak 104 continuously increased with the amount of LiCoO_2 . The respective XRD patterns in FIG. 11 have been adjusted for 2-theta zero point position

- 22 -

and normalized in intensity for comparison (shown in the insert in the right side of FIG. 11). The gradient coated samples were also evaluated electrochemically for rate capability and first cycle efficiency as listed in Table 1, according to protocol 1.

5 Example 9. Comparison of LiCoO_2 -coated $\text{Li}_{1.05}\text{NiO}_2$ Core Material.

Three gradient coated $\text{Li}_{1.05}\text{NiO}_2$ materials were synthesized and coated with 5 %, 10 % and 15 % LiCoO_2 using the methods as substantially described in Examples 4 and 7. The coated samples were tested electrochemically for rate capability and first cycle efficiency as described above and protocol 1. The specific capacity results, listed in Table 2, show that
10 lithium cobalt oxide coated lithium nickel oxide compounds of the present invention can provide better or at least equal performance capacity compared to non-coated compounds.

FIG. 9 shows the ASI of a cell utilizing the LiCoO_2 -coated $\text{Li}_{1.05}\text{NiO}_2$ material, measured according to protocol 3 above and FIG. 10 shows several ASI measurements of a cell utilizing uncoated LiMgNiO_2 material. As shown in FIGS. 9 and 10, the performance, in
15 terms of potential available power, of the lithium-cobalt-oxide coated lithium-nickel-oxide cells is comparable, if not better than cells utilizing the uncoated lithium-nickel-oxide materials. FIG. 12 shows the capacity retention at a discharge rate of about 1C of cells utilizing various active materials including lithium-nickel oxide, lithium magnesium nickel oxide, lithium-cobalt-oxide coated lithium magnesium nickel oxide, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$
20 (CA1505 cell available from TODA Co., Japan), and LiCoO_2 (C-5 grade available from Nippon Chemical Industrial Co., LTD., Tokyo, Japan). The results presented in FIG. 12 indicate that the cells utilizing the coated and uncoated lithium-magnesium-nickel oxides of the invention can have better performance compared to cells utilizing lithium cobalt oxide. FIG. 13 is a graph showing the differential scanning calorimetry of the uncoated and lithium-
25 cobalt oxide-coated lithium-magnesium-nickel oxide material of the present invention compared to a commercially available lithium-nickel-cobalt oxide material at about a 100 % state of charge and shows that the coated and uncoated materials are more thermally stable.

Those skilled in the art should appreciate that the parameters and configurations described herein are exemplary and that actual parameters and/or configurations will depend
30 upon the specific application in which the systems and methods of the present invention are use. Those skilled in the art should recognize or be able to ascertain, using no more than routine experimentation, equivalents to the specific embodiments of the invention. For example, the shape of the particles of the present invention, in either the coated or uncoated

- 23 -

embodiments, can include particles shaped to facilitate packing and/or increase packing and/or tap density such as, but not limited to, plates or having one dimension substantially greater than a second and/or third dimension. Further, a range or combination of particle sizes can also be utilized. For example, a mixture of lithium cobalt oxide coated lithium magnesium nickel oxide particles with uncoated lithium magnesium nickel oxide particles can be utilized in the systems, device, and techniques of the present invention wherein the mixture can have a first type or kind of particle, e.g. uncoated, having a first particle size and a second type or kind of particle, e.g. coated and/or a different Mg loading, having a second particle size. It is therefore to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described. Further, it is to be appreciated various alterations, modifications, and improvements will readily occur to those skilled in the art. Such alterations, modifications, and improvements are intended to be part of this disclosure, and are intended to be within the spirit and scope of the invention. Moreover, the present invention is directed to each feature, system, or method described herein and any combination of two or more features, systems, and/or methods, if such features, systems, or methods are not mutually inconsistent, is considered to be within the scope of the present invention as embodied in the claims. The use of the clarifiers such as “first” and “second” or even “third” and “fourth” is intended to modify an element and does not create an implication of priority, precedent, sequence, or temporal order, over another but is intended as labels.

What is claimed is:

- 24 -

CLAIMS

1. A composition having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$ wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.9 < x + y < 1.3$.
- 5 2. The composition of claim 1, wherein $0.9 < x < 1.1$.
3. The composition of claim 1 wherein $0.02 < y < 0.05$.
- 10 4. The composition of claim 1 wherein $x = 1.05$ and $y = 0.025$.
5. A composition comprising:
a core having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$ wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.9 < x + y < 1.3$; and
15 a coating on the core having a formula $\text{Li}_a\text{Co}_b\text{O}_2$ wherein $0.7 < a < 1.3$, and $0.9 < b < 1.2$.
6. The composition of claim 5 wherein $0.9 < a < 1.3$ and $0.9 < b < 1.2$.
- 20 7. The composition of claim 5 wherein the molar ratio of Co:Ni ranges between about 0.01 to about 0.8.
8. The composition of claim 5 wherein $0.9 < x < 1.1$ and $0.02 < y < 0.05$.
- 25 9. The composition of claim 8 wherein $x = 1.05$ and $y = 0.025$.
10. An electrochemical cell comprising a cathode comprising a composition having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$ wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.9 < x + y < 1.3$.
- 30 11. The electrochemical cell of claim 10 wherein $0.9 < x < 1.1$.
12. The electrochemical cell of claim 11 wherein $0.02 < y < 0.05$.

- 25 -

13. The electrochemical cell of claim 10 wherein $x = 1.05$ and $y = 0.025$.

14. An electrochemical cell comprising a cathode comprising particles comprising a core having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$, wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.9 < x + y < 1.3$ and a coating on the core, the coating having a formula $\text{Li}_a\text{Co}_b\text{O}_2$ wherein $0.7 < a < 1.3$, and $0.9 < b < 1.2$.

15. The electrochemical cell of claim 14 wherein $0.9 < x < 1.1$, $0.02 < y < 0.05$, $0.9 < a < 1.3$, and $0.9 < b < 1.2$.

16. The electrochemical cell of claim 15 wherein $x = 1.05$ and $y = 0.025$, $a = 1$, and $b = 0.025$.

17. A method of preparing a composition comprising:
providing a mixture of compounds comprising a lithium source, a magnesium source, and a nickel source; and
sintering the mixture in an oxidizing atmosphere at a temperature and for a period sufficient to crystallize the mixture into a $\text{Li}_x\text{Mg}_y\text{NiO}_2$ composition, wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.9 < x + y < 1.3$.

18. The method of claim 17 wherein the magnesium source comprises $\text{Mg}(\text{OH})_2$, the lithium source comprises LiNO_3 and LiOH , and the nickel source comprises $\text{Ni}(\text{OH})_2$.

19. The method of claim 17 wherein the temperature is between about 400°C and 950°C .

20. The method of claim 17 wherein sintering comprises heating the mixture at a rate of about 5°C per minute to a first soaking temperature of between about 400°C and 500°C .

21. The method of claim 20 wherein sintering further comprises maintaining the first soaking temperature for about four hours.

- 26 -

22. The method of claim 20 wherein sintering further comprises heating the mixture at a rate of about 2° C per minute to a second soaking temperature of between about 600° C and 900° C.

5 23. The method of claim 22 wherein sintering further comprises maintaining the second soaking temperature for about four hours.

24. A method of preparing coated particles comprising steps of:
providing a first mixture of compounds comprising a lithium source, a magnesium
10 source, and a nickel source and sintering the first mixture in an oxidizing atmosphere at a first temperature and for a first period sufficient to crystallize the first mixture into core particles having a formula $\text{Li}_x\text{Mg}_y\text{NiO}_2$ wherein $0.9 < x < 1.3$, $0.01 < y < 0.1$, and $0.91 < x + y < 1.3$; and
coating the core particles with a second mixture comprising compounds comprising
15 lithium and cobalt and sintering the coated core particles at a second temperature and for a second period sufficient to crystallize the coating having a formula $\text{Li}_a\text{Co}_b\text{O}_2$ wherein $0.7 < a < 1.3$, and $0.9 < b < 1.2$.

25. The method of claim 24 wherein $0.9 < x < 1.1$, $0.02 < y < 0.05$, $0.9 < a < 1.3$, and
20 $0.9 < b < 1.2$.

26. The method of claim 24 wherein sintering the first mixture comprises heating the first mixture at a rate of about 5° C per minute to a first soaking temperature of between about 400° C and 500° C and heating the first mixture at a rate of about 2° C per minute to a second
25 soaking temperature of between about 600° C and 900° C.

27. The method of claim 26 wherein sintering the first mixture further comprises maintaining the first soaking temperature for about one to about six hours and maintaining the second soaking temperature for about one to about eight hours.

30

28. The method of claim 24 wherein sintering the coated core particles comprises heating the coated core particles at a rate of about 2° C per minute to a third soaking temperature of between about 90° C and about 120° C.

- 27 -

29. The method of claim 28 wherein sintering the coated core particles further comprises maintaining the third soaking temperature for about one hour.

5 30. The method of claim 29 wherein sintering the coated core particles further comprises heating the coated core particles at a rate of about 5° C per minute to a fourth soaking temperature of between about 400° C and about 500° C.

31. The method of claim 30 wherein sintering the coated core particles further comprises
10 maintaining the fourth soaking temperature for about one hour.

32. The method of claim 24 wherein sintering the coated core particles further comprises heating the coated core particles at a rate of about 2° C per minute to a fifth soaking temperature of between about 600° C and about 900° C.

15 33. The method of claim 32 wherein sintering the coated core particles further comprises maintaining the fifth soaking temperature for about two hours.

34. The method of claim 24 wherein the magnesium source comprises $\text{Mg}(\text{OH})_2$, the
20 lithium source comprises LiNO_3 and LiOH , and the nickel source comprises $\text{Ni}(\text{OH})_2$.

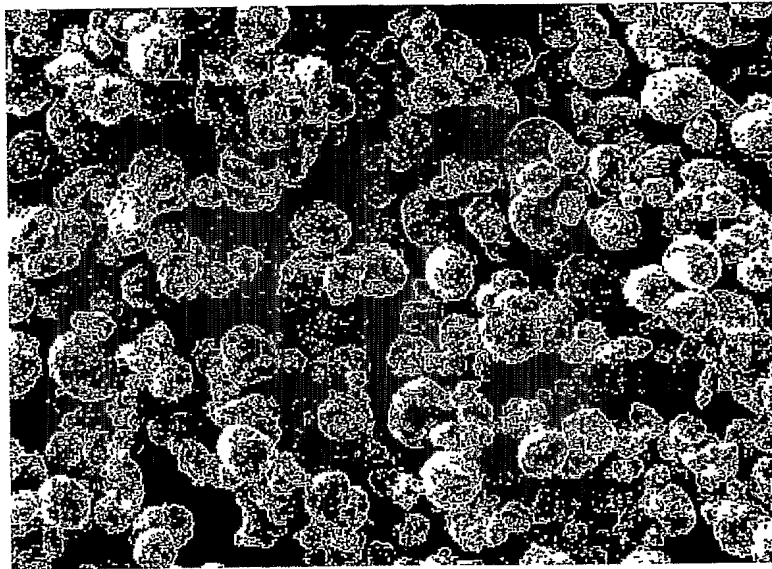
35. A particle comprising a core material having a composition of a formula
 $\text{Li}_{1-y}\text{Mg}_y\text{NiO}_2$ where Mg and Li are predominantly in a crystallographic 3a site and Ni is
predominantly in a crystallographic 3b site and $0.01 < y < 0.1$.

25 36. An electrochemical cell using the particle of claim 35.

37. The particle of claim 35 further comprising a coating layer on the core material, the
coating layer comprising a material having a formula $\text{Li}_a\text{Co}_b\text{O}_2$, $0.7 < a < 1.3$, $0.9 < b < 1.2$.

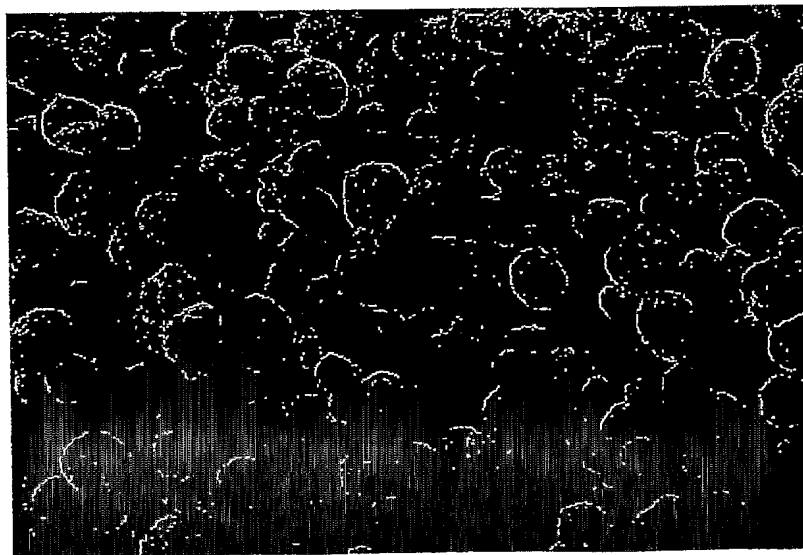
30 38. The particle of claim 37 wherein the coating layer is less than about 30 wt% of the particle.

1/12



500X

FIG. 1



500X

FIG. 4

2/12

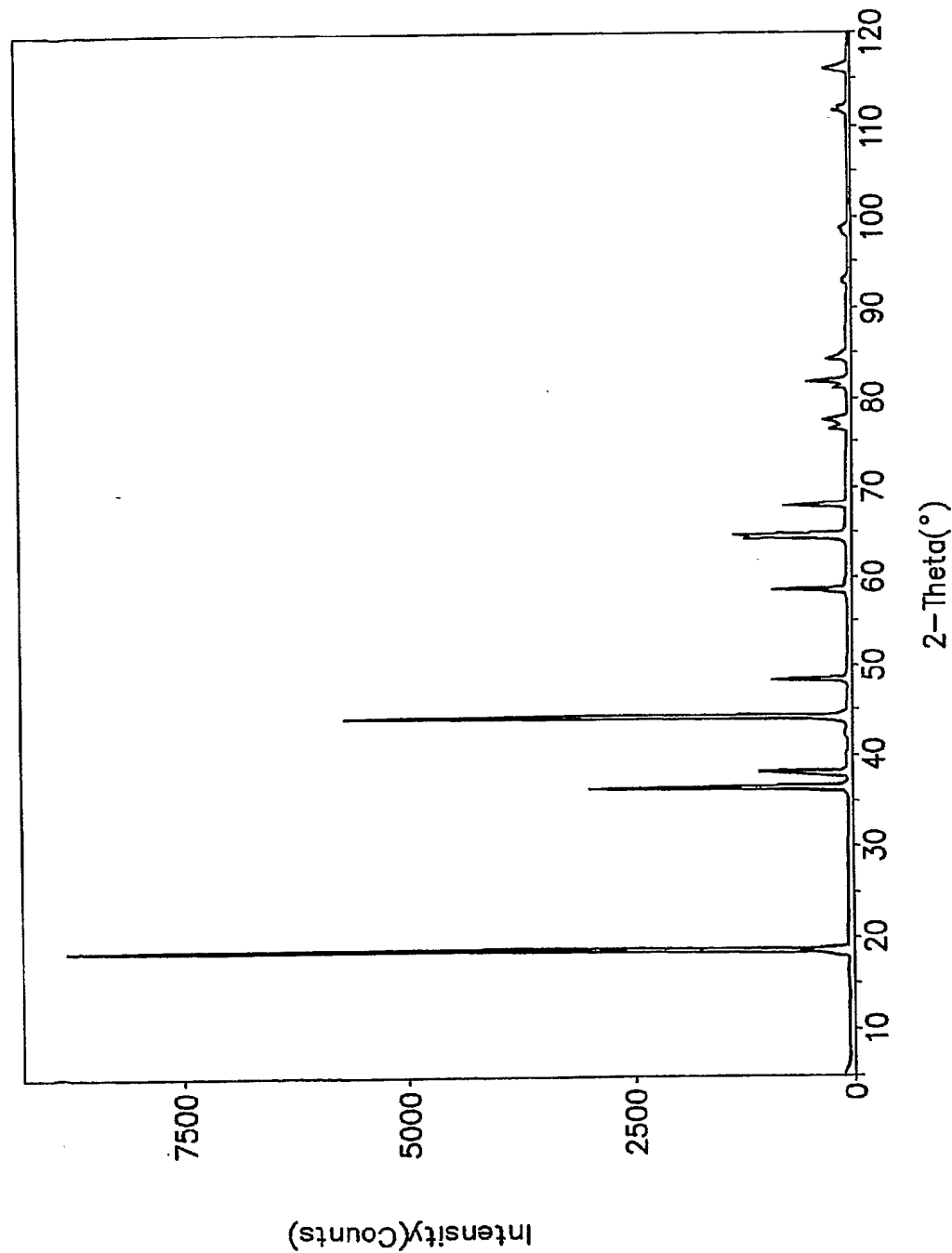


FIG. 2

3/12

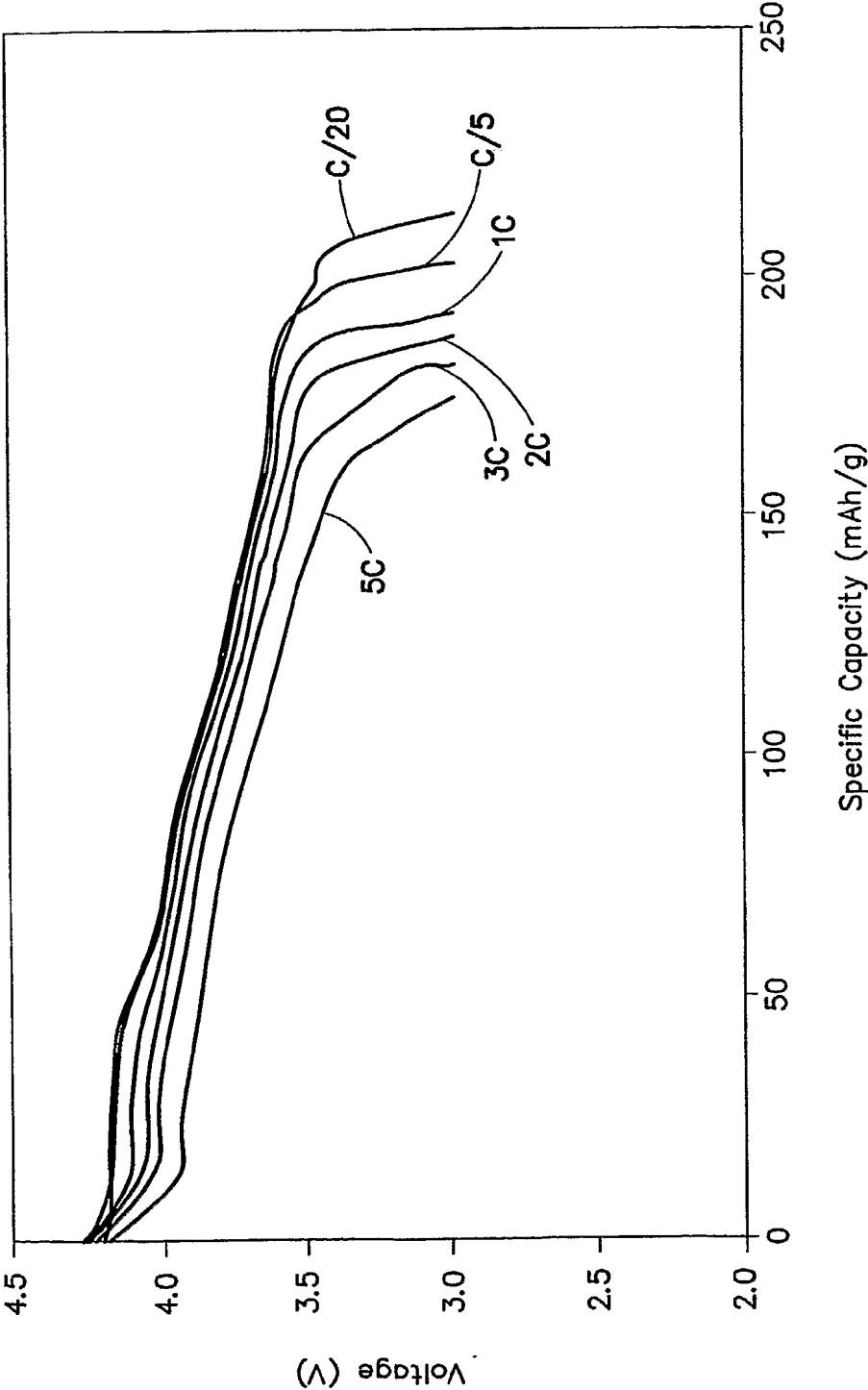


FIG. 3

4/12

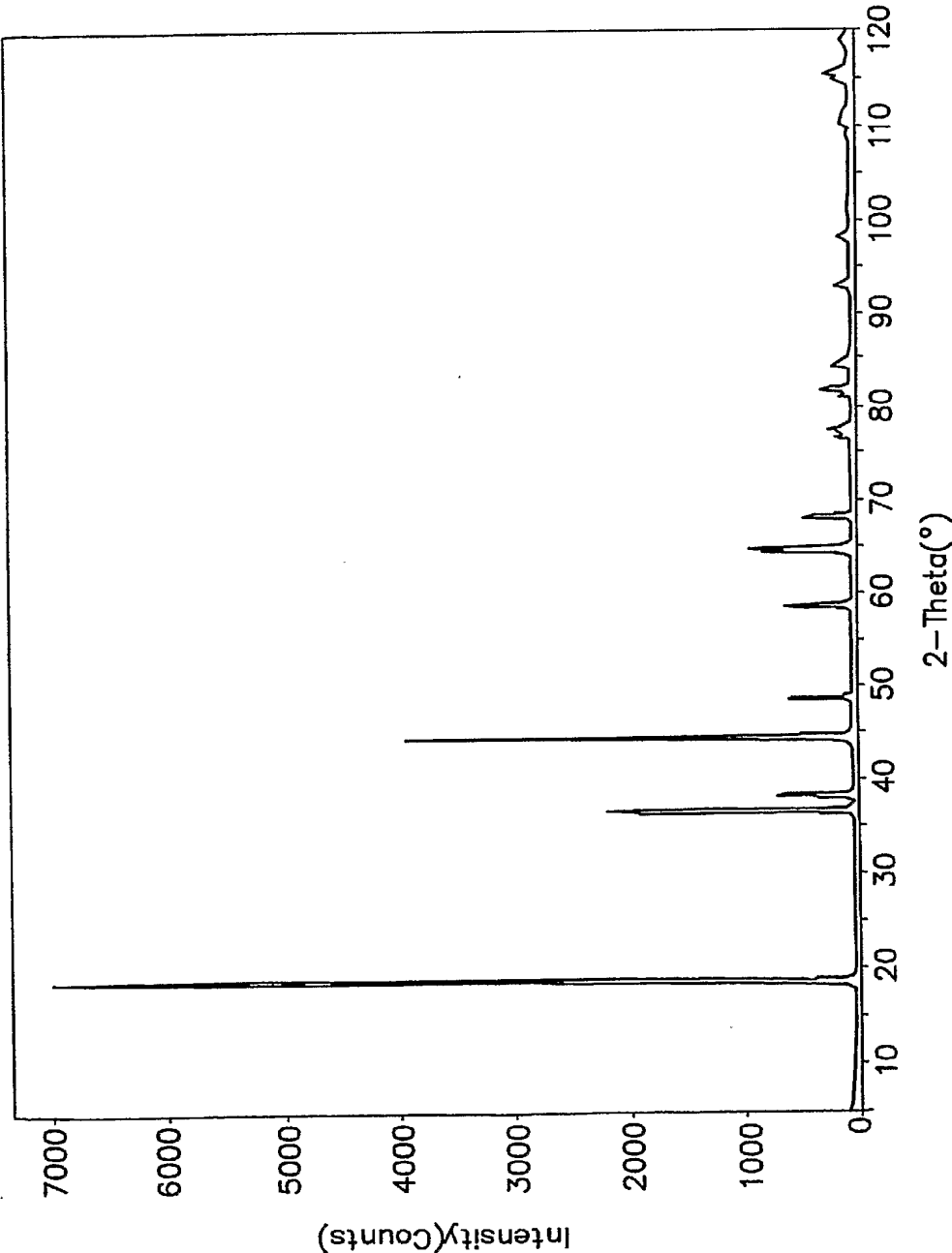


FIG. 5

5/12

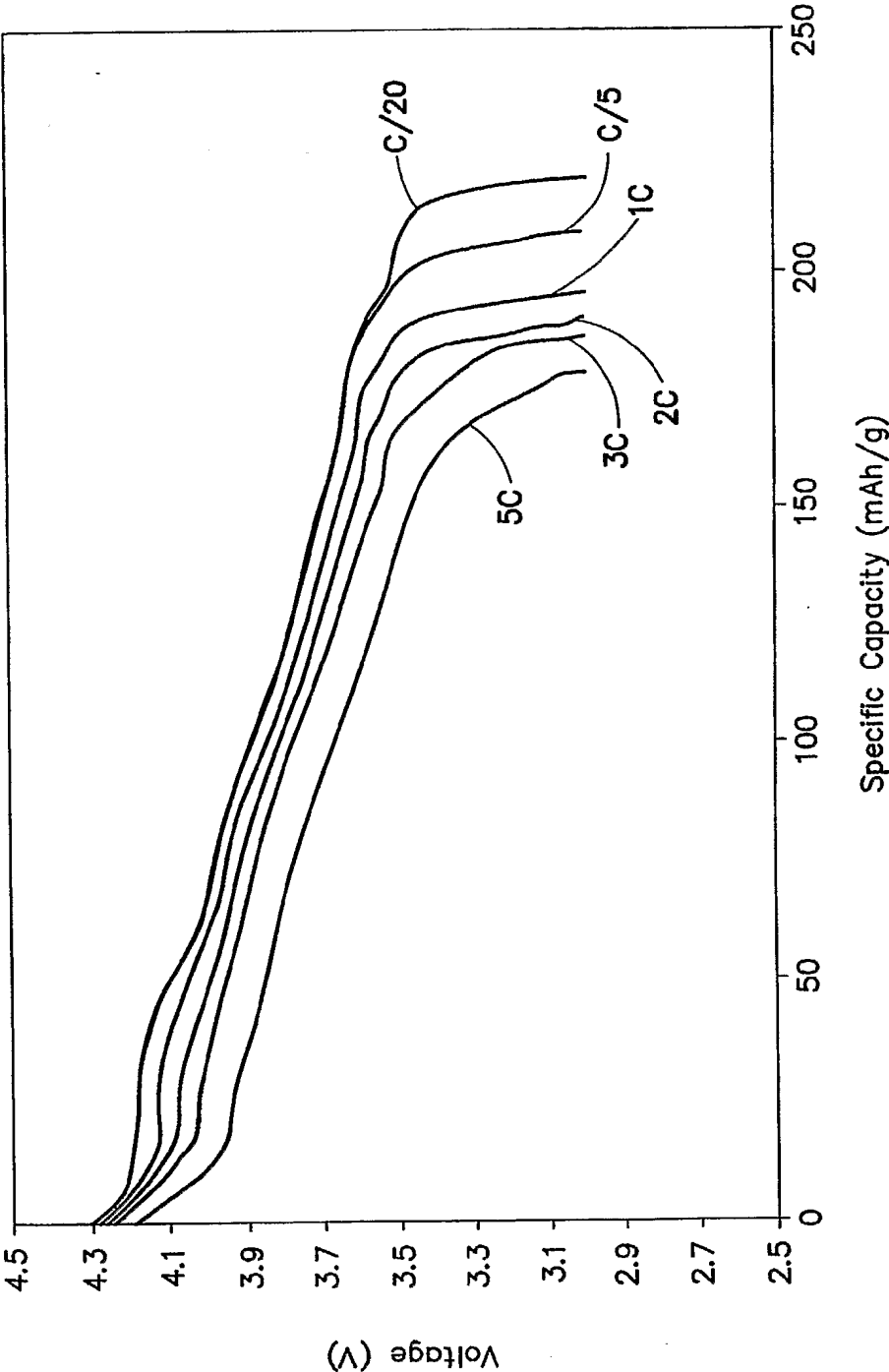
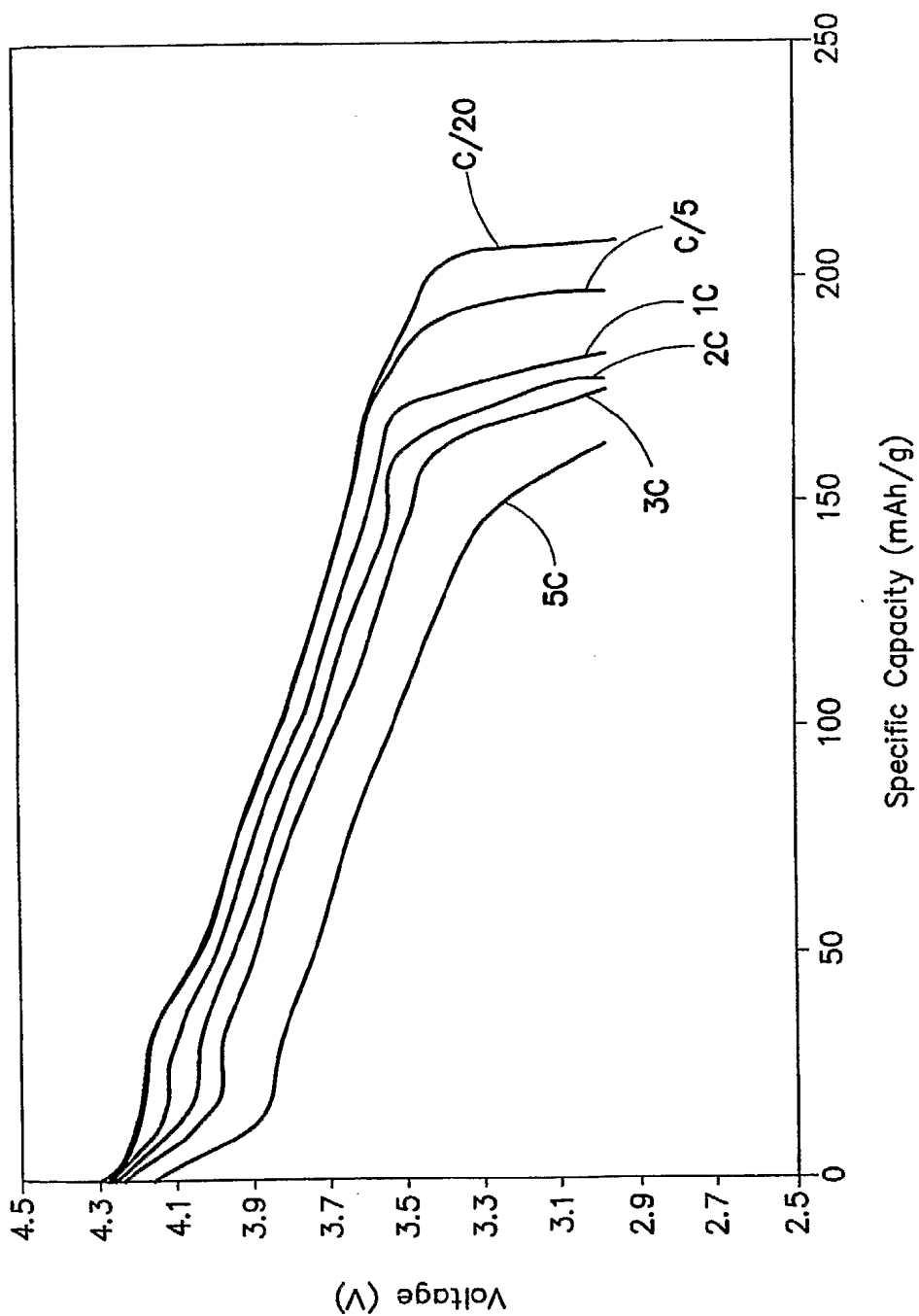


FIG. 6

6/12

**FIG. 7**

7/12

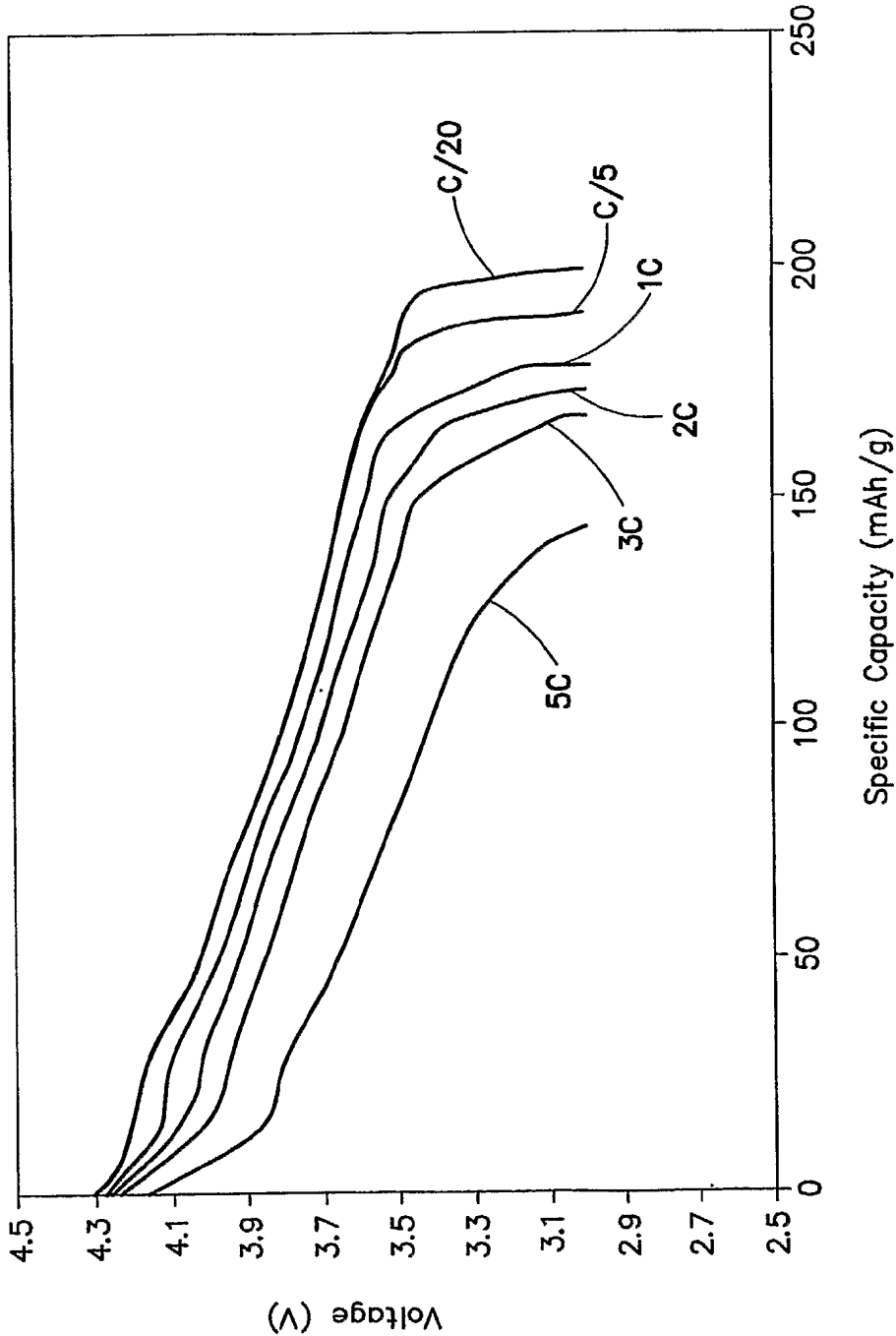


FIG. 8

8/12

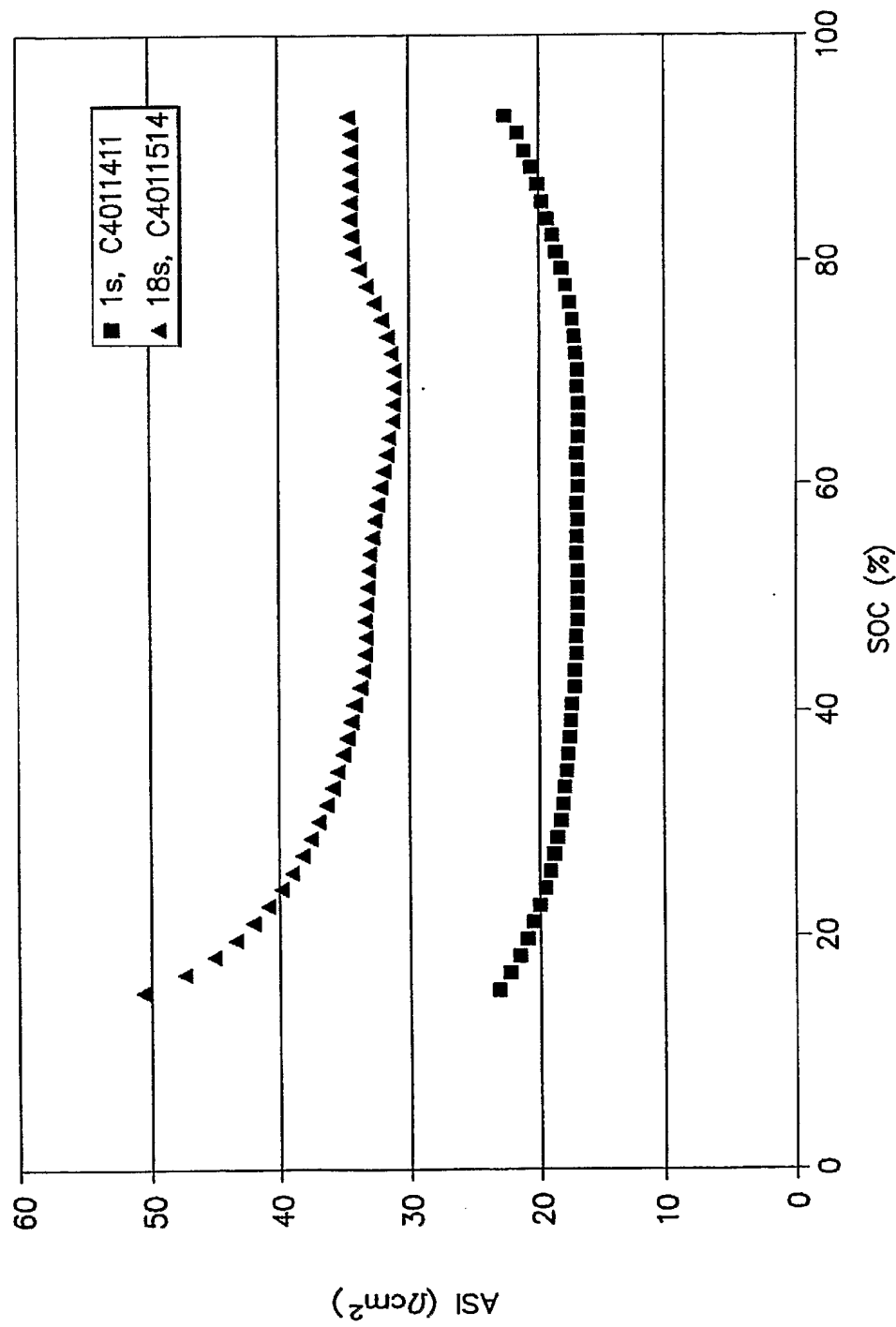


FIG. 9

9/12

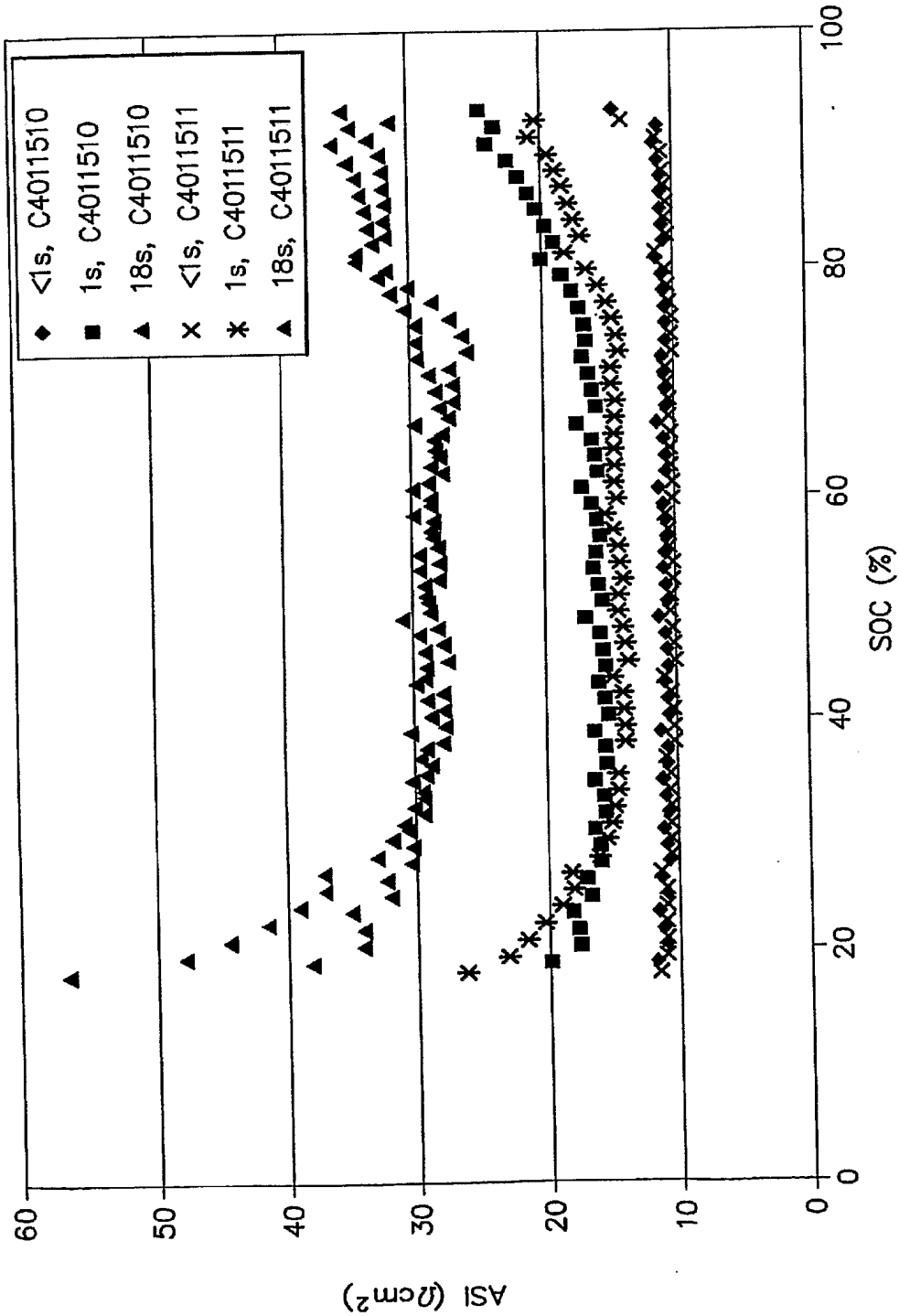


FIG. 10

10/12

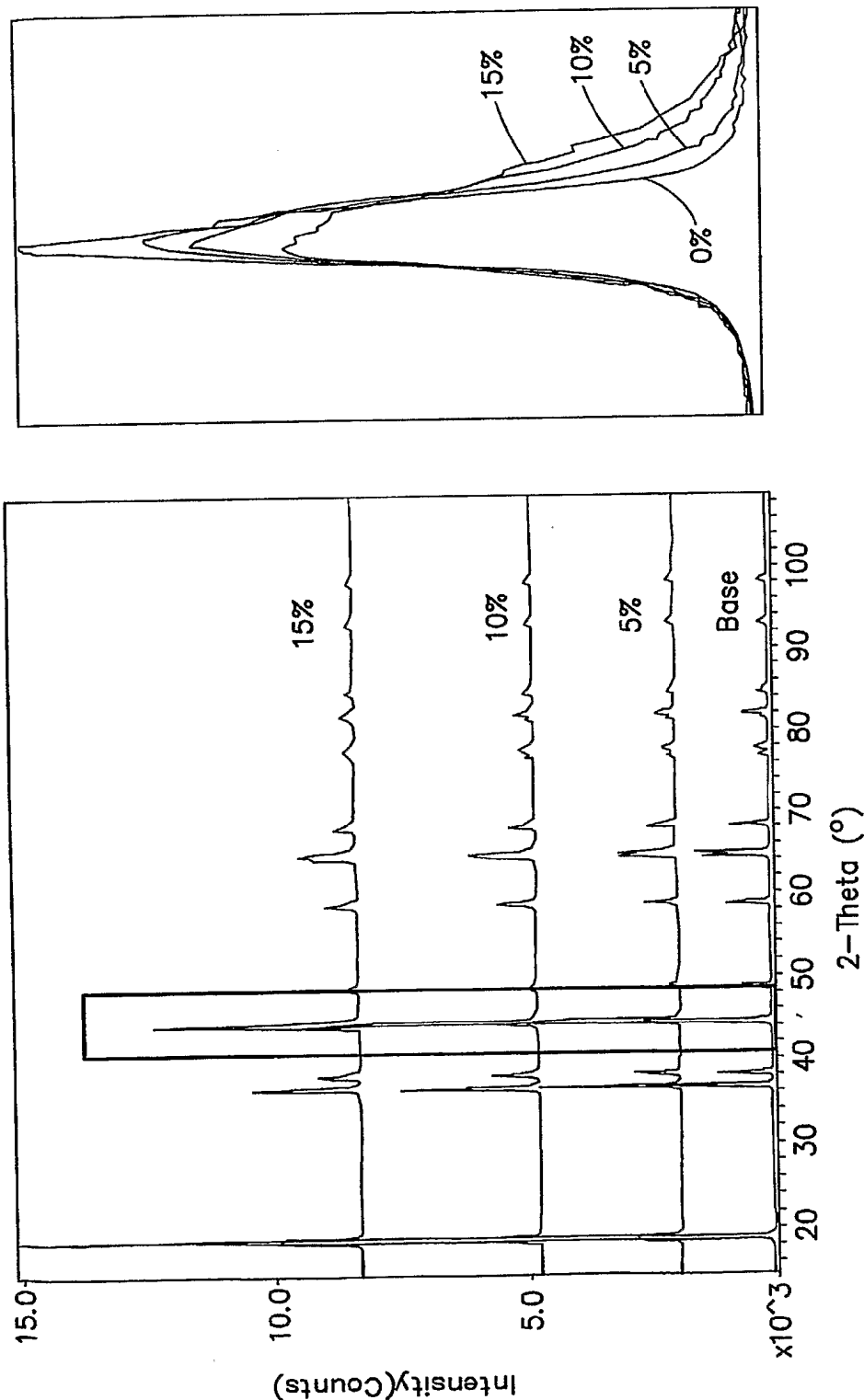


FIG. 11

11/12

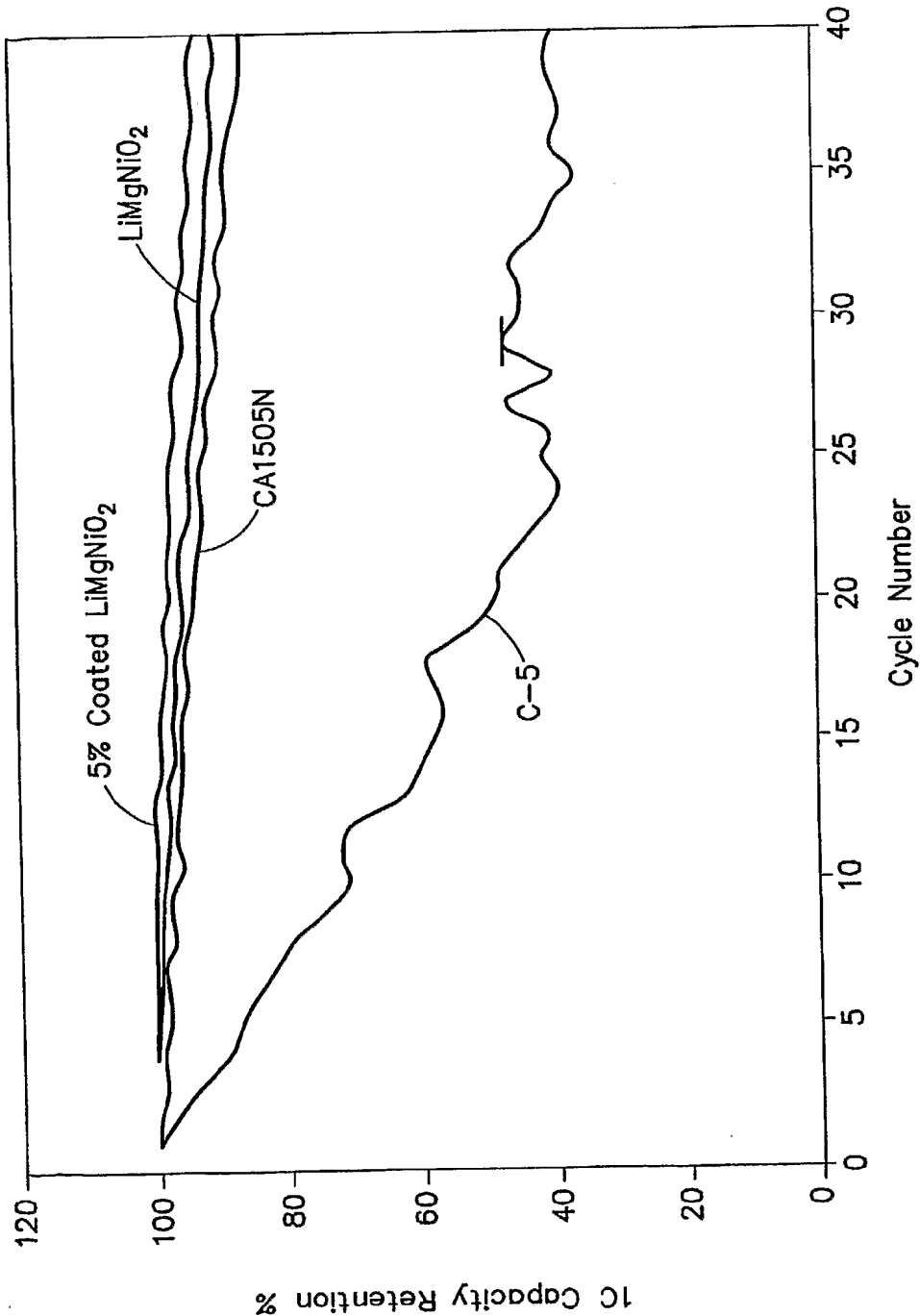


FIG. 12

12/12

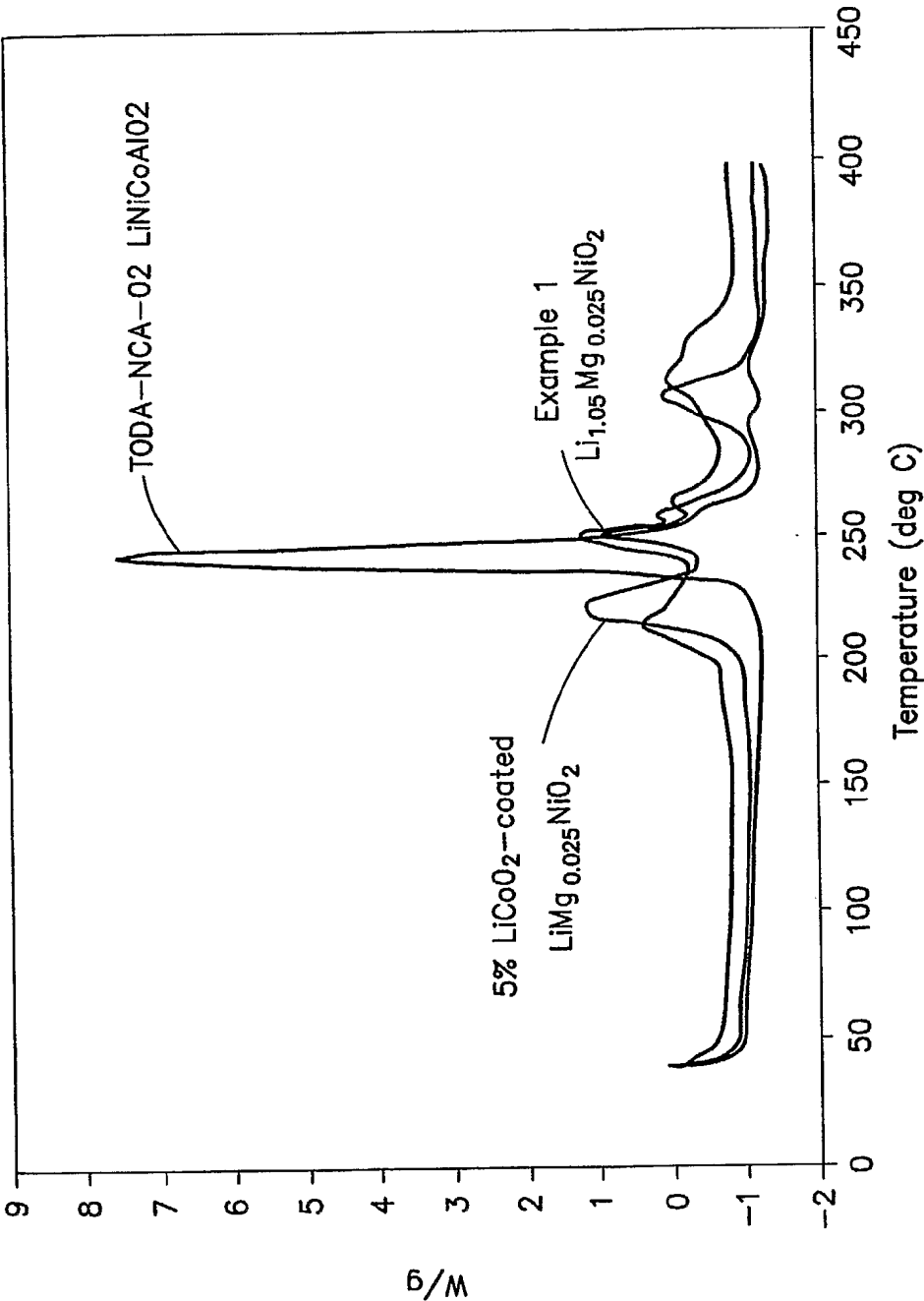


FIG. 13

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/017548

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M4/48 H01M4/58

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)
IPC 7 C01G H01M

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

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

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 986 116 A (TDK CORPORATION) 15 March 2000 (2000-03-15)	1-4, 10-13, 17-23, 35, 36
Y	abstract paragraphs '0023! - '0031! ----- -/--	5-9, 14-16, 24-34, 37, 38

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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 document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

30 August 2005

Date of mailing of the international search report

06/09/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Kelly, M

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/017548

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 744 780 A (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD) 27 November 1996 (1996-11-27)	1-4, 10-13, 17-23, 35,36
Y	claim 6 page 4, lines 37-42 abstract	5-9, 14-16, 24-34, 37,38
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 02, 29 February 2000 (2000-02-29) -& JP 11 310416 A (CARNEGIE MELLON UNIV), 9 November 1999 (1999-11-09)	1-4, 10-13, 17-23, 35,36
Y	the whole document	5-9, 14-16, 24-34, 37,38
Y	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 06, 30 June 1997 (1997-06-30) -& JP 09 050810 A (MITSUI TOATSU CHEM INC), 18 February 1997 (1997-02-18) the whole document	1-38
Y	US 6 071 649 A (MAO ET AL) 6 June 2000 (2000-06-06) abstract column 2, lines 47-60 column 3, line 44 - column 5, line 46	1-38
Y	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 08, 30 June 1999 (1999-06-30) & JP 11 067209 A (SANYO ELECTRIC CO LTD), 9 March 1999 (1999-03-09) abstract	1-38
Y	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 14, 31 December 1998 (1998-12-31) & JP 10 236826 A (SAKAI CHEM IND CO LTD), 8 September 1998 (1998-09-08) abstract	1-38
A	US 6 045 771 A (MATSUBARA ET AL) 4 April 2000 (2000-04-04) cited in the application abstract	1-38

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2005/017548

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0986116	A	15-03-2000	AU 7452098 A EP 0986116 A1 US 6361822 B1 WO 9854772 A1 JP 11045716 A	30-12-1998 15-03-2000 26-03-2002 03-12-1998 16-02-1999
EP 0744780	A	27-11-1996	JP 3079033 B2 JP 9274917 A DE 69633038 D1 DE 69633038 T2 EP 0744780 A1 JP 3260282 B2 JP 9092285 A US 5631105 A	21-08-2000 21-10-1997 09-09-2004 30-12-2004 27-11-1996 25-02-2002 04-04-1997 20-05-1997
JP 11310416	A	09-11-1999	NONE	
JP 09050810	A	18-02-1997	NONE	
US 6071649	A	06-06-2000	NONE	
JP 11067209	A	09-03-1999	NONE	
JP 10236826	A	08-09-1998	NONE	
US 6045771	A	04-04-2000	CA 2209933 A1 DE 69620154 D1 DE 69620154 T2 EP 0806397 A1 WO 9719023 A1 JP 3130813 B2 JP 10069910 A	29-05-1997 02-05-2002 02-10-2002 12-11-1997 29-05-1997 31-01-2001 10-03-1998

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
27 December 2002 (27.12.2002)

PCT

(10) International Publication Number
WO 02/103824 A2(51) International Patent Classification⁷: H01M 4/52,
C01G 53/04

(21) International Application Number: PCT/JP02/05897

(22) International Filing Date: 13 June 2002 (13.06.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/298,791 15 June 2001 (15.06.2001) US
60/298,798 15 June 2001 (15.06.2001) US
10/073,674 11 February 2002 (11.02.2002) US

(71) Applicant: KUREHA CHEMICAL INDUSTRY COMPANY, LIMITED [JP/JP]; 1-9-11, Nihonbashi Horidomecho, Chuo-ku, Tokyo 103-8552 (JP).

(72) Inventors: ONNERUD, Christina, Lampe; 449 Salem End Road, Framingham, MA 01702 (US). ONNERUD, Per; 449 Salem End Road, Framingham, MA 01702 (US). SHI, Jie; 12 Marion Road, Acton, MA 01720 (US). DALTON, Sharon; 339 Lynn Street, #2, Malden, MA 02148

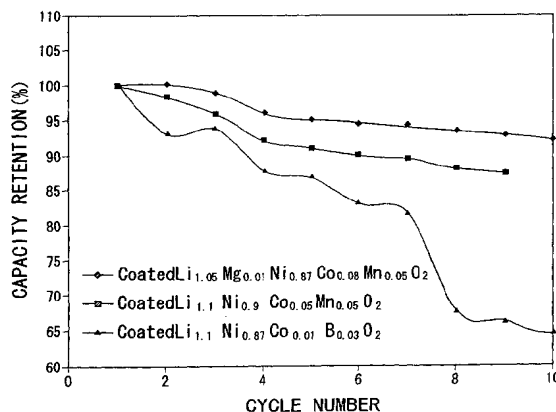
(US). KOIZUMI, Tomoyoshi; 5-7-5, Nakaoka-machi, Iwaki-shi, Fukushima 974-8251 (JP). NAGAI, Aisaku; 2-2-12, Hon-cho, Ueda-machi, Iwaki-shi, Fukushima 974-8261 (JP).

(74) Agent: ENDO, Yukio; TOKO INTERNATIONAL PATENT OFFICE, Hasegawa Bldg. 4F, 7-7, Toranomon 3-chome, Minato-ku, Tokyo 105-0001 (JP).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: GRADIENT CATHODE MATERIAL FOR LITHIUM RECHARGEABLE BATTERIES



(57) **Abstract:** A composition suitable for use as a cathode material of a lithium battery includes a core material having an empirical formula $\text{Li}_x\text{M}'_z\text{Ni}_{1-y}\text{M}''_y\text{O}_2$. "x" is equal to or greater than about 0.1 and equal to or less than about 1.3. "y" is greater than about 0.0 and equal to or less than about 0.5. "z" is greater than about 0.0 and equal to or less than about 0.2. M' is at least one member of the group consisting of sodium, potassium, nickel, calcium, magnesium and strontium. M'' is at least one member of the group consisting of cobalt, iron, manganese, chromium, vanadium, titanium, magnesium, silicon, boron, aluminum and gallium. A coating on the core has a greater ratio of cobalt to nickel than the core. The coating and, optionally, the core can be a material having an empirical formula $\text{Li}_x\text{A}_{x2}\text{Ni}_{1-y1-y2}\text{Co}_{y1}\text{B}_{z1}\text{O}_a$. "x1" is greater than about 0.1 and equal to or less than about 1.3. "x2," "y1" and "z1" each is greater than about 0.0 and equal to or less than about 0.2. "a" is greater than 1.5 and less than about 2.1. "A" is at least one element selected from the group consisting of barium, magnesium, calcium and strontium. "B" is at least one element selected from the group consisting of boron, aluminum, gallium, manganese, titanium, vanadium and zirconium.



WO 02/103824 A2



Published:

— without international search report and to be republished
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

- 1 -

DESCRIPTION

GRADIENT CATHODE MATERIAL
FOR LITHIUM RECHARGEABLE BATTERIES

5

[TECHNICAL FIELD]

The invention relates to a composition and a method of forming a composition, the composition being suitable for employment in a cathode of a lithium battery.

10 The invention also relates to a lithium battery that employs a cathode material of the invention.

[BACKGROUND ART]

Lithium-based batteries are used in a variety of applications, such as VTRs, communication devices and portable devices of any type. Traditionally, the lithium battery industry has employed LiCoO_2 -type materials as the active component of lithium battery cathodes. However, LiCoO_2 lithium battery cathodes typically are very expensive and exhibit relatively low capacity, such as a capacity of about 140mAh/g.

One alternative to the use of LiCoO_2 -based cathode materials is LiNiO_2 -based materials, which generally are less expensive, but exhibit higher capacities, such as capacities in excess of about 170mAh/g. Typically, LiNiO_2 -based materials employed in lithium battery cathodes have a nickel content of about 80% and a cobalt content of about 20% (atomic weight percent). However,

25

- 2 -

LiNiO₂-based materials generally are less safe (i.e. exhibit more gassing) than are LiCoO₂-type materials. Further, LiNiO₂-based materials exhibit a first cycle efficiency that often is between about five and about ten percent lower than that of LiCoO₂-based cathodes. Generally, LiCoO₂-based materials have efficiencies in a range of between about 93% and about 96%, whereas LiNiO₂-based materials have efficiencies that range from between about 83% to about 88%.

Therefore, a need exists for cathode materials suitable for use in lithium-based batteries that minimize or overcome the above-referenced problems.

[DESCLOSURE OF INVENTION]

The invention generally is directed to a composition and a method of forming a composition, the composition being suitable for employment in a cathode of a lithium battery. The invention also is directed to a lithium battery that employs a cathode material of the invention.

In one embodiment, the invention is a composition that includes a core having an empirical formula of $\text{Li}_x\text{M}'_z\text{Ni}_{1-y}\text{M}''_y\text{O}_2$. "x" is greater than about 0.1 and equal to or less than about 1.3. "y" is greater than about 0.0 and equal to or less than about 0.5. "z" is greater than about 0.0 and equal to or less than about 0.2. M' is at least one member of the group consisting of sodium (Na), potassium (K), nickel (Ni), calcium (Ca), magnesium (Mg) and strontium (Sr). M'' is at least one member of the group consisting of

- 3 -

cobalt (Co), iron (Fe), manganese (Mn), chromium (Cr), vanadium (V), titanium (Ti), magnesium (Mg), silicon (Si), boron (B), aluminum (Al) and gallium (Ga). A coating on the core has a greater ratio of cobalt to nickel than the core.

5 In a specific embodiment, the coating on the core has an empirical formula of $\text{Li}_{x1}\text{A}_{x2}\text{Ni}_{1-y1-z1}\text{Co}_{y1}\text{B}_z\text{O}_a$. "x1" is greater than about 0.1 and equal to or less than about 1.3. "x2," "y1" and "z1" each is greater than 0.0 and equal to or less than about 0.2. "a" is greater than about 1.5 and less than about 2.1. "A" is at least one element selected from the group consisting of barium, magnesium, calcium and strontium. "B" is at least one element selected from the group consisting of boron, aluminum, gallium, manganese, titanium, vanadium and zirconium.

15 A method of forming a composition includes drying a water solution of LiNO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in which a core material is immersed, said core material having an empirical formula $\text{Li}_x\text{M}'_z\text{Ni}_{1-y}\text{M}''_y\text{O}_2$. x is greater than about 0.1 and equal to or less than about 1.3, "y" is greater than about 0.0 and equal to or less than about 0.5, and z is greater than about 0.0 and equal to or less than about 0.2. M' is at least one member of the group consisting of sodium, potassium, nickel, calcium, magnesium, and strontium. M'' is at least one member of the group consisting of cobalt, iron, manganese, chromium, vanadium, titanium, magnesium, silicon, boron, aluminum and gallium. Evaporation of water from the solution causes formation of a precursor

- 4 -

coating on the core material. Thereafter, the precursor coating is calcined to thereby form the composition.

The compositions of the claimed invention generally will exhibit improved capacity, cyclability and safety over LiCoO_2 and LiNiO_2 counterparts. Further, these compositions typically are less expensive to manufacture than LiCoO_2 -based materials. Also, the capacity, cyclability and safety of materials employed as cathodes can be manipulated by employing different combinations of dopants in the coating to substitute for lithium and nickel in certain embodiments of the invention. The gradient material on the other hand typically has a matched lattice, which enables a fully functional material similar to the regular oxides in cycling properties, which enables the material to stay intact throughout the life of the battery.

[BRIEF DESCRIPTION OF THE DRAWINGS]

Figure 1 is a cross section view of a lithium-based battery of the invention and a cathode of the invention.

Figure 2 is a three dimensional representation of a crystal structure of the invention.

Figures 3A through 3C are representations of oxygen, metal and combined oxygen and metal planes in a crystal structure having the empirical formula LiMO_2 projected along the (012) plane.

Figures 4A and 4B represent charge density, top ($x=1$, Figure 4A) and bottom ($x=0$, Figure 4B), of a Li_xNiO_2 crystal structure.

- 5 -

Figure 5 is a representation of charge density in the metallic planes of Li_xNiO_2 for $x=1$.

Figure 6 is a representation of charge density in metallic planes for Li_xNiO_2 for $x=0$.

5 Figure 7 is a plot of c-axis length versus lithium content (x) in LiCoO_x as determined theoretically, and as identified by experiment.

Figure 8 is a plot of c-axis length versus lithium content (x) in LiNiO_2 as theoretically predicted.

10 Figure 9 is a plot of voltage (V) versus specific capacity (mAh/g), identified as polarization curves of three materials: LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and $\text{Li}_{1.05}\text{Mg}_{0.5}\text{Ni}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$.

15 Figure 10 is an x-ray powder diffraction pattern of a gradient material of the invention described in Example 1.

Figure 11 is an x-ray powder diffraction pattern of the gradient material having an asymmetry peak of Example 1.

20 Figure 12 is an x-ray powder diffraction pattern of a gradient material of the invention described in Example 2.

Figure 13 is an x-ray powder diffraction pattern of an asymmetric peak of the gradient material of Example 2.

Figure 14 is an x-ray powder diffraction pattern of a gradient material of the invention described in Example 3.

25 Figure 15 is an x-ray powder diffraction pattern of an asymmetric peak of the gradient material described in Example 3.

- 6 -

Figure 16 is an x-ray powder diffraction pattern of a cathode material described in Comparative Example 1.

Figure 17 is an x-ray powder diffraction pattern of a cathode material described in Comparative Example 2.

5 Figure 18 is an x-ray powder diffraction pattern of a powder that includes a mixed cathode material from Comparative Example 3, wherein peaks from LiCoO_2 peaks from $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ are identified.

10 Figure 19 is an x-ray powder diffraction pattern of a material described in Comparative Example 4.

Figure 20 are x-ray powder diffraction patterns of a Bragg reflection (104) from Example 17.

Figure 21 is a plot of first cycle efficiency versus Ni ion disorder.

15 Figure 22 is a plot of first cycle efficiency versus oxygen stoichiometry.

Figure 23 shows the capacity retention for non-coated samples of Examples 6, 15 and 16.

20 Figure 24 shows capacity retention for coated samples in Examples 9, 19 and 20.

[DESCRIPTION OF PREFERRED EMBODIMENTS]

25 The above features and other details of the invention now will be described more particularly with reference to the accompanying drawings and pointed out in the claims. It will be understood that the particular embodiments of the invention are shown by way of illustration and not as limitations of the invention. The

- 7 -

principal features of this invention can be employed in various embodiments without departing from the scope of the invention.

The present invention generally is directed to a composition, having a core and a coating. The core has an empirical formula of $\text{Li}_x\text{M}'_z\text{Ni}_{1-y}\text{M}''_y\text{O}_2$. The coating on the core has a greater ratio of cobalt to nickel than the core.

In one embodiment, the coating has the empirical formula of: $\text{Li}_{x1}\text{A}_{x2}\text{Ni}_{1-y1-z1}\text{Co}_{y1}\text{B}_{z1}\text{O}_a$. The crystal structure of the core, and optionally of the coating, is of an "α-NaFeO₂-type" and can be characterized as having a hexagonal lattice within the R-3m group. The composition of the invention is suitable for employment as the active material in cathodes for rechargeable lithium-ion or lithium polymer-type batteries, among other uses. The invention also generally is directed to lithium batteries and to cathodes of lithium batteries that employ the composition of the invention, and to methods of forming the composition.

In one embodiment of the invention, the composition include a core having an empirical formula $\text{Li}_x\text{M}'_z\text{Ni}_{1-y}\text{M}''_y\text{O}_2$, wherein "x" is greater than about 0.1 and equal to or less than about 1.3, "y" is greater than about 0.0 and equal to or less than about 0.5, and "z" is greater than about 0.0 and equal to or less than about 0.2. M' is at least one member of the group consisting of sodium, potassium, nickel, calcium, magnesium and strontium. "M" is at least one member of the group consisting of cobalt, iron,

- 8 -

manganese, chromium, vanadium, titanium, magnesium, silicon, boron, aluminum and gallium. A coating on the core has a greater ratio of cobalt to nickel than the core.

In a specific embodiment, M" includes cobalt. In
5 another embodiment, "y" is in a range of between about 0.1 and 0.5. In a particularly preferred embodiment, "y" is about 0.1. In another particularly preferred embodiment, "y" is about 0.2.

In another embodiment, M' includes magnesium.
10 In another specific embodiment, M' includes magnesium and M" includes boron. In still another embodiment, M" includes manganese. In one particularly preferred embodiment, M" includes cobalt and boron and, optionally, M' includes magnesium. In another embodiment, M"
15 includes cobalt and manganese, and, optionally, M' includes magnesium. In still another especially preferred embodiment, the sum of "x" and "z" equals about 1.

Generally, the ratio of cobalt to nickel of the composition of the invention increases as a gradient from
20 the core to an outer surface of the coating.

In another embodiment, the core material has an empirical formula $\text{Li}_x\text{Ni}_{0.9-y}\text{Co}_{0.1+y}\text{O}_2$. "x" is greater than about 0.1 and equal to or less than 1.3. "y" is greater than zero and equal to or less than about 0.4.

25 In still another embodiment, the core material has an empirical formula, $\text{Li}_x\text{Mg}_z\text{Ni}_{1-y}\text{Co}_y\text{B}_v\text{O}_2$. "x" is greater than about 0.1 and equal to or less than about 1.3. "y" is

- 9 -

greater than 0.0 and equal to or less than about 0.4. "v" is equal to or less than about 0.4. "B" is at least one member of the group consisting of manganese, boron, aluminum and gallium.

5 In a specific embodiment of the invention, the core material includes $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. In another embodiment, the core material includes $\text{Li}_{1.1}\text{Ni}_{0.87}\text{Co}_{0.1}\text{B}_{0.03}\text{O}_2$.

 In still another embodiment of the invention, the coating has an empirical formula $\text{Li}_{x1}\text{A}_{x2}\text{Ni}_{1-y1-z1}\text{Co}_{y1}\text{B}_{z1}\text{O}_a$.
10 "x1" is greater than about 0.1 and equal to or less than about 1.3. "x2," "y1" and "z1" each is greater than about 0.0 and equal to or less than about 0.2. "a" is greater than about 1.5 and less than about 2.1. "A" is at least one element selected from the group consisting of barium, magnesium,
15 calcium and strontium. "B" is at least one element selected from the group consisting of boron, aluminum, gallium, manganese, titanium, vanadium and zirconium. In one preferred embodiment, "A" is magnesium and "B" is aluminum. In another preferred embodiment, "A" is
20 magnesium and "B" is manganese.

 In one embodiment, the invention is a composition, such as a crystal, wherein a core and a coating of the composition each has an empirical formula:
 $\text{Li}_{x1}\text{A}_{x2}\text{Ni}_{1-y1-z1}\text{Co}_{y1}\text{B}_{z1}\text{O}_a$, wherein "x1" is greater than about
25 0.1 and equal to or less than about 1.3, "x2," "y1" and "z1" each is greater than about 0.0 and equal to or less than about 0.2, and "a" is greater than about 1.5 and less than

- 10 -

about 2.1. "A" is at least one element selected from the group consisting of barium, magnesium, calcium and strontium, and "B" is at least one element selected from the group consisting of aluminum, gallium, manganese, titanium, vanadium and zirconium. The coating has a greater ratio of cobalt to nickel than the core. In one preferred embodiment, "A" is magnesium and "B" is aluminum. In another preferred embodiment, "A" is magnesium and "B" is manganese. In still another embodiment, "A" is magnesium and "B" is gallium.

In another embodiment, the invention is a method of forming a composition. The method includes evaporating water from a solution of LiNO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in which a core material is immersed. The core material has the empirical formula of the composition of the invention. Evaporation of water from the solution causes formation of a precursor coating on the core material. The precursor coating then is calcined to thereby form the composition of the invention. In one embodiment, the amount of coating formed on the core is greater than 0.0 mole percent and less than about 15.0 mole percent of the resulting core and coating. In another embodiment, the amount of coating formed on the core is greater than 5.0 mole percent and less than about 15.0 mole percent of the resulting core and coating. In still another embodiment, the amount of coating formed on the core is greater than 5.0 mole percent and less than about 10.0 mole percent of the resulting core

- 11 -

and coating.

In one embodiment, the stoichiometric ratio of LiNO_3 to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the solution is in range of between about 0.0 and about 1.2. In another embodiment, the precursor coating is calcined by heating the coating to a temperature in a range of between about 500°C and about 900°C for a period of time in a range of between about 0.2 hours and about 12 hours.

In a preferred embodiment, the precursor coating is calcined by heating the coating and the core material at a rate in a range of between about 5°C and about 100°C per minute to a temperature in a range of between about 300°C and about 500°C, which temperature then is maintained for a period of time in a range of between about 0.2 hours and about 4 hours. The precursor coating and the core material then are heated at a rate of between about 5°C and about 50°C per minute to a temperature of between about 600°C and about 900°C, at which temperature the coating then is maintained for a period of time in a range of between about 0.2 hours and about 12 hours.

In another embodiment, the invention is a cathode formed of a composition of the invention suitable for use in a lithium battery. In another embodiment, the invention is a lithium battery employing a cathode that includes a composition of the invention.

A lithium-based battery of the invention, such as a lithium ion battery, a lithium polymer battery, or a lithium

- 12 -

battery, is shown partly in cross-section in Figure 1. As shown therein, lithium-based battery 10 includes case 12. Case 12 is formed of a suitable material, such as stainless steel. Insulator 14 is located at a bottom portion of case 12.

5 Electrode group 16 includes cathode 18, separator 20, and anode 22. Anode 22 also is an embodiment of the invention. Insulating seal plate 24 at an upper opening of case 12 is fixed to case 12 by a suitable method, such as by caulking. Cathode terminal 26 at a central portion of insulating seal

10 plate 24 is connected electrically to cathode lead 28. Cathode lead 28, in turn, is connected electrically to cathode 18 of electrode group 16. Anode 22 of electrode group 16 is connected electrically to case 12 as an anode terminal, via a negative electrode lead (not shown).

15 Lithium-based battery 10 includes several electrode groups, all of which have the same construction. Insulating paper 30 is located above electrode group 16 and has a central opening.

Cathode 18 of the invention includes a composition

20 of the invention as an active material. Cathode 18 also includes a suitable conductive agent, such as acetylene black, carbon black and graphite. A binder, such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), ethylene-propylene-diene copolymer (EPDM) or

25 styrene-butadiene rubber (SBR), also is included in cathode 18. The ratios of active material, conductive agent and binder can be, for example, about 80 to 96 weight percent of

- 13 -

the active material, about 2 to 20 weight percent of the
conductive agent, and about 2 to 7 weight percent of the
binder. The mixed active material, conductive agent and
binder are suspended in an appropriate solvent and then
5 coated onto a suitable collector. Examples of suitable
collectors are aluminum foil. The composition then is dried
to form a thin plate on the collector. Cathodes suitable for
use in lithium-based batteries are well-known in the art.
Examples of suitable positive electrodes are described in EP
10 0 688 057 B1, EP 0 573 266 A1, EP 0 763 865 A1, the
teachings all of which are incorporated herein by reference
in their entirety.

Separator 20 includes a suitable polymer, such as
a synthetic resin non-woven fabric, a polyethylene porous
15 film, a porous PVDF film or a polypropylene porous film, or a
suitable glass fiber. Materials suitable for use as separator
20 in a lithium ion battery are well-known in the art, such as
is described in the references incorporated by reference
above.

20 Anode 22 includes a coating on a collector. A
suitable collector can be formed of, for example, copper foil.
The coating includes a polymer component, carbon graphite
or hard carbon (amorphous carbon) and an additive. The
polymer binder component is a suitable material, such as
25 polyvinylidene fluoride (PVDF), polyimide (PI) and
polyvinylidene fluoride-hexafluoropropylene copolymer
(PVDF-HFP). The polymer binder typically is present in the

- 14 -

coating in an amount in a range of between about 1 and about 10 weight percent.

A suitable additive is carbon black or small particulate graphite flakes. An example of a suitable amount of additive in a coating is in a range of between about 0.5 and about 7 percent by weight.

Although not wishing to be bound by any particular theory, the crystal structure of crystals of the invention is believed to be of " α -NaFeO₂-type," and is in the following described in a hexagonal lattice within a "R-3m" space group. In this structure, Li and "A" atoms occupy the so-called "3a" site in the structure ($x=0$, $y=0$, and $z=0$), the Ni and "B" atoms occupy the "3b" site ($x=0$, $y=0$, $z=0.5$), and oxygen occupies the "6c" site ($x=0$, $y=0$, $z=z$). The "z" coordinate of oxygen changes depending on the nature of "A" and "B" elements and their relative ratios. Typically the "z" coordinate is between 0.22 and 0.26. The cell parameters of this material, "a" and "c," also vary with the chemical composition. Typically, cell parameters are found between the following ranges: $a=2.75 - 2.95 \text{ \AA}$, and $c=13.9 - 14.3 \text{ \AA}$. Generally, the cell parameters exhibit a gradient through the particle structure. Also there is a gradient of diminishing nickel concentration from the core to the surface of each particle. The gradient particulate structure typically produces a diffraction pattern that has asymmetric Bragg reflection peaks when subjected to X-ray diffraction (XRD). This peak asymmetry is a "fingerprint" of the

- 15 -

gradient material of the invention and provides experimental evidence that the material has a gradually changing elemental composition.

Coatings of the cathode materials of the current invention can improve the safety of Ni-based materials at the same time as capacity is maintained or improved, although the Ni-atoms are diluted. This is made possible by the simultaneous substitution of atoms in both the Li-site (3a site) and the Ni-site (3b site). "A" atoms partly substitute for Li atoms in the 3a site. "B" atoms substitute for Ni in the 3b site. Further, the capacity and cyclability is higher due to higher stabilization of the structure than that found in the LiCoO_2 system. This means that more lithium can be removed from the structure without having a structural collapse. It is believed that safety is high compared to LiNiO_2 due to shielding of the 3b-3b interaction, which is the dominating mode for structural collapse. This enables less structure damage upon cycling and higher stability at the lower Li contents at about $x=0.2$, which is the traditional cut-off for the LiNiO_2 systems, especially for compounds containing about 20% Co. Polarization behavior of the composition of the invention can lead to higher capacity for devices that utilize a 3.5 volt cut-off for the electronics.

Characteristics of the cathode materials of the invention relate to capacity, cyclability, and safety. For example, compositions of the invention can exhibit different capacities depending on the charge/discharge rate and

- 16 -

other external conditions, such as electrolyte choice and electrode formulation. "Capacity" is defined herein as the number of Li ions that can reversibly be removed from the crystal structures of lithium-based materials, such as those
5 of the invention. "Reversibility," as defined herein, means that the structure substantially maintains its integrity and that Li can be intercalated back to restore the initial crystal structure. In theory, this is the definition of capacity at an infinitely small rate.

10 "Safety," as defined herein, means structural stability or structural integrity; if a material decomposes during cycling or is easily decomposed or causes gassing at elevated temperatures, the material is considered unsafe. Polarization behavior adds yet another dimension to
15 capacity. Materials having a high voltage profile will have improved capacity especially when discharge ends at 3.5V, which is a technology constraint for many semiconductive electronic circuits. This is the case for cellular phones, for example, wherein typically one lithium battery cell is used,
20 but less of a concern for other devices, such as laptop computers, that utilize multiple batteries.

Based on the lithium content, capacities of both LiCoO_2 and LiNiO_2 should be just about equal, since they contain the same amount of Li ions. Practically this is not
25 the case. The LiCoO_2 material allows only about 50% Li extraction while in LiNiO_2 one can reversibly remove about 80% of Li ions. After this critical amount of Li is removed,

- 17 -

the crystal structure of a metal oxide irreversibly changes, i.e. a structural collapse takes place. The structural collapse is not preferred in a Li-ion battery as it contributes to capacity degradation and lower cyclability. The
5 over-charge is also a safety concern.

The structural reason for this collapse is described below. The crystal structure of layered LiMO_2 is shown in Figure 2. Intuitively, it is not obvious that the crystal in Figure. 2 will collapse, i.e. drastically reduce the distance
10 between the MO_2 layers, when Li ions are removed from the structure. One would expect that the negatively charged neighbors (oxygen atoms) repel after the positively charged ions are removed. This should cause quite an opposite effect; the crystal should expand. However, this is shown
15 not to be the case. Instead it is instructive to look at in the (012) family of crystallographic planes in the LiMO_2 structure, which are shown in Figure. 2. The sequence of these planes is depicted in Figure. 3. The crystal consists of alternating slightly distorted hexagonal metal/oxygen
20 layers. The metal layer consists of both Li and M (Co/Ni/B) atoms, while the oxygen layer contains only oxygen atoms. This view of the structure helps to understand why the crystal is not repelling when the Li-ion layers are removed even in a simplistic ionic model. In fact, as seen from
25 Figure 3, when the Li atoms are removed from the structure, M-atoms still remain in the metal plane and keep the structure stable.

- 18 -

The crystal is kept together by interaction of oxygen and metal planes. The metal planes consist of alternating rows of Li/A and Ni/Co/B atoms. When Li atoms are removed, the metal plane becomes partially
5 depopulated, which should result in an overall decrease in structural stability. Another conclusion that we have drawn simply from structural considerations is that, when Li is removed, it leaves behind a quasi 1 -dimensional string of M(Ni,Co,B) atoms in the (012) plane which should be
10 thermodynamically less stable and thus should have a strong tendency to diffuse into sites that were formerly occupied by Li atoms.

A quantum mechanical approach has been used to support the statements just made. Figure 4A depicts the
15 charge density (i.e. chemical bonding of the structure) in the oxygen layer of a LiNiO₂ crystal, while in Figure. 4B the charge density of a nickel oxide crystal is presented when all Li ions are removed from the structure.

The charge density of Li_xNiO₂ in (012) metal planes
20 is presented in Figure 5 for x=1, and in Figure 6 for x=0. Top part of Figure 5 shows rows of Li atoms (smaller circles) and Ni atoms (larger circles). Li atoms do not have any covalent bonding with their nearest neighbors; they are surrounded by very low-density charge regions. This
25 means that Li is fully donating its valence electron to the crystal and ionically interacts with other atoms. On the contrary, Ni atoms create strong covalent bonds in their

- 19 -

respective row, as is also seen in the Figure. 5. For $x=1$, the Ni-Ni interaction between different rows is negligible, screened completely by Li-ions.

When Li is removed from the structure, as shown in
5 Figure 6, the picture changes drastically. Ni-Ni bonds are created between the Ni rows in the (012) planes. These metal-metal bonds are responsible for Ni disorder. Therefore, a certain amount of "shielding" atoms has to be preserved in the structure to limit the process of creation of
10 such bonds on the level above which the structural collapse occurs. This is the reason for introducing other atoms than Li (A atoms) in the novel compounds. These atoms stabilize the crystal, as they are normally not removed during cycling.

Shielding is achieved through doping of Li sites by
15 "less mobile" ions, possibly with larger ionic radii.

The change in the c-axis length upon Li deintercalation has been modeled. The results for Li_xCoO_2 are presented in Figure. 7. A drastic change in the slope of the $c(x)$ function takes place at around $x=0.5$, which
20 coincides with the maximum degree of Li deintercalation from LiCoO_2 . It is believed that this change shows the limit for stability in the crystal structure and determines the maximum capacity of a cathode material. In other words, the slope of the $c(x)$ function in the low- x region is an
25 indicator of relative capacity of a material, i.e. when this slope is larger, the "critical point" in x moves towards lower x values, indicating greater stability of a material. The

- 20 -

c-axis change for LiNiO_2 also was modeled, and is shown in Figure. 8. The change in the slope of $c(x)$ for LiNiO_2 takes place at much lower values of x , indicating increased capacity due to the increased structural stability of LiNiO_2 as compared to LiCoO_2 . The underlying physics behind this behavior is believed to be based on the fact that Ni has one electron more than Co. This additional electron occupies so-called antibonding sites, which counteract the tendency to collapse the structure by Ni-Ni bonds, shown in Figure. 5. This feature is used as a rationale for doping with B atoms. It is believed that doping of B atoms into Ni sites lowers the number of electrons that are occupying antibonding orbitals, thereby improving safety due to the dilution of Ni atoms. However, due to the compromised capacity, "A" atoms are used to further stabilize the structure, thereby allowing relatively high capacity while maintaining safety. Further, due to the increased structural stability, cyclability typically is high.

During discharge, polarization of an active cathode material is especially important. For instance, in cellular telephones, traditionally electronics has stopped working at voltages below 3.5V. For this application it is important that as much capacity as possible is available above this limit. Figure 9 shows a polarization comparison between LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ oxide materials. As can be seen from Figure 9, the total capacity of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ material is higher if the cell is allowed to discharge below

- 21 -

3.5V. However, if 3.5V is the cut-off voltage during discharge, LiCoO_2 would have a relatively better capacity. This feature also is addressed in the current invention. We have found certain dopants to increase voltage during
5 discharge. Elements that will positively influence the voltage profile when doped on the 3b site (B atoms) are among the preferred elements. Elements that increase polarization compared to pure LiNiO_2 oxide when substituted on the 3b site are manganese, boron, aluminum,
10 gallium and cobalt. Manganese exhibits a particularly good effect on safety properties, while high capacity can be maintained for low substitution levels.

The invention now will be further and specifically described by the following examples, which are not intended
15 to be limiting. All parts and percentages are by weight unless specified otherwise.

[EXAMPLES]

A gradient coated material can be prepared by employing LiNO_3 (crystalline aggregates, made by Alfa Aesar)
20 and $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (crystalline, made by Alfa Aesar) used in stoichiometric amounts to produce a coated precursor material. So far, the base materials (the core) have been a commercially available nickel based material and material synthesized at Arthur D. Little, Inc. Laboratories.
25 Commercial materials are available from, for instance, FMC or Nippon Chemical (Japan). The Li and Co precursors are dissolved in distilled water and mixed with powdered base

- 22 -

material. The water then is evaporated off on a hot plate while stirring during a time period of 4 hours. The precursor-coated material then is sintered in air using a Degussa-Ney muffle furnace (model 3-550 or 3-1750) under the following profile: ramp 5°C/minute, 450°C for 1 hour, ramp 2°C/minute, 700-800°C for 2 hours. This allows a concentration gradient structure to form that has more cobalt at the surface than at the core. The invention is not limited to this particular synthesis method, but it is preferred that the core material is coated by a non-reacted precursor from lithium and cobalt precursors in a molten or dissolved state.

All samples are cooled to room temperature by shutting off the furnace and allowing natural cooling. The furnace, therefore, is programmed to shut off after the profile above has been executed. The sintered product is ground for 5 minutes in a Retsch/Brinkmann mortar grinder (model RM100) fitted with an agate mortar and pestle. The particle size distribution ranges between 1-50µm after grinding.

Materials purity, lattice constants and peak asymmetry are measured by XRD (x-ray diffraction) using a Shimadzu 6000 X-ray powder diffractometer, supplied by Kratus Analytical.

Example 1

Synthesis of 10% (mol/mol) LiCoO_2 gradient having a $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ core. (i.e., a gradient product formed by

- 23 -

calcining a coated material of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ core coated with 10% (mol/mol) of LiCoO_2 precursor)

7.06g LiNO_3 and 29.69g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 150 ml distilled H_2O to which 100 g N-82 (LiNi_{0.6}Co_{0.2}O₂) was added. The H_2O was evaporated off on a hotplate during stirring. The obtained dried cake was ground for 5 minutes in the mortar grinder, placed in an alumina crucible, and sintered under the following heating profile: ramp 5°C/minute to 450°C, hold at 450°C for 1 hour, ramp 2°C/minute to 750°C, and hold for 1 hour. The sample was then allowed to cool naturally to room temperature and ground for 5 minutes to break up agglomerates. When subjected to the XRD, this material shown to have a gradient profile. No impurities were visible, as can be seen in XRD pattern of Figure 10. The lattice parameters were $a=2.8676(6)\text{Å}$, $c=14.168(2)\text{Å}$. Peak asymmetry by XRD was present in the sample, Figure 11.

Electrochemical measurements of this powder yielded a specific capacity of 172mAh/g with a cycle efficiency of 92%, and a gassing volume of 4.5cc/g. This shows the material to have improved gassing characteristics and cycle efficiency to Comparative Example 2.

Example 2

Synthesis of 2.5% (mol/mol) LiCoO_2 gradient having a LiNi_{0.8}Co_{0.2}O₂ (N-82, Nippon Chemical) core.

1.77g LiNO_3 , and 7.42g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 100ml distilled H_2O to which 100g N-82 was

- 24 -

added. The H₂O was evaporated off on a hot plate during stirring. The obtained dried cake was ground for 5 minutes in the mortar grinder, placed in an alumina crucible, and sintered under the following heating profile: ramp
5 10°C/minute to 110°C, hold at 110°C for 20 minutes, ramp
5°C/minute to 450°C, hold at 450°C for 1 hour, ramp
2°C/minute to 700°C, and hold for 1 hour. The sample
then was allowed to cool naturally to room temperature and
ground for 5 minutes to break up agglomerates. When
10 subjected to XRD, this material was shown to have a
gradient profile. No impurities were visible (Figure 12).
Peak asymmetry by XRD was present in the sample, Figure.
13.

Electrochemical measurements of this powder
15 yielded a specific capacity of 148mAh/g with a cycle
efficiency of 82%, and a gassing volume of 1.8cc/g. This
shows the material to have improved gassing characteristics
when compared to Comparative Example 2.

Example 3

20 Synthesis of 10% (mol/mol) LiCoO₂ gradient having a
Li_{1.1}Ni_{0.87}Co_{0.1}B_{0.03}O₂ (Arthur D. Little material (ADL)) core.

7.11g LiNO₃ and 29.98g Co(NO)₃ · 6H₂O were
dissolved in 150ml distilled H₂O to which 100g
Li_{1.1}Ni_{0.87}Co_{0.1}B_{0.03}O₂ (ADL) was added. The H₂O was
25 evaporated off on a hot plate during stirring. The obtained
dried cake was ground for 5 minutes in the mortar grinder,
placed in an alumina crucible, and sintered under the

- 25 -

following heating profile: ramp 5°C/minute to 450°C, hold at 450°C for 1 hour, ramp 2°C/minute to 750°C, and hold for 1 hour. The sample then was allowed to cool naturally to room temperature and ground for 5 minutes to break up agglomerates. When subjected to XRD this material was shown to have a gradient profile. No impurities were visible (Figure 14). The lattice parameters were $a=2.873(2)$, $b=c=14.167(5)$, and slight peak asymmetry by XRD was present in the sample, Figure. 15.

Electrochemical measurements of this powder yielded a specific capacity of 181mAh/g with a cycle efficiency of about 91%, and a gassing volume of 6.0cc/g when cycled between 4.2V and 3.0V. This shows the material to have improved gassing and cycle efficiency characteristics to Comparative Example 4.

Example 4

Example for electrode fabrication and electrochemical measurement

37.6 grams metal oxide powder (active engineered gradient material and N-82, LiCoO_2 comparisons), 1.2 gram Chevron C-100 carbon black (conductive additive), and 18 grams NMP were added in a 250 ml jar with 50 steel balls (diameter= $\frac{1}{4}$ inch). The mixture was mixed by paint shaking for 30 min. 10 g PVDF (polyvinylidene fluoride) binder solution (Kureha Chemical LFD 2777, 12wt% PVDF solution) was added. The mixture was further mixed for 10 minutes.

- 26 -

The slurry was applied on an Al foil (thickness of about 20 μ m) using a doctor blade with a wet coating thickness 10 mil. The coated electrode was heated at 130°C for 30min. The typical thickness of the electrode with Al
5 current collector was 100 μ m.

The electrode was cut in 2 cm² disc. The disc was pressed at room temperature with an apparent pressure of 500 kg/cm². The typical thickness of the electrode with the current collector after pressing was 80 μ m, and the typical
10 active material weight in the disc electrode was 20mg. The electrode was dried at 80°C under vacuum for 16 hours before cell assembly.

A 2-electrode coin cell was fabricated using lithium foil (Aldrich) as counter and the dried electrode as working
15 electrode, glass fiber as separator, and EC/DMC (1:1)-LiPF₆ 1M (EM Industries) as electrolyte. All operations were carried in an Ar filled glove box with water and oxygen level less than 1ppm.

The coin cell was cycled using Maccor Systems
20 cyler using charge currents (de-intercalation) to 4.30V and then constant charge voltage (at 4.30V) to a current less than 50 μ A/cm². Discharge used C/20 and C/5 discharge currents to a voltage 3.0V, wherein e.g., C/20 represents a current density at which the whole capacity was discharged
25 in 20 hours.

Example 5

Example for gassing measurements

- 27 -

a) Cell Fabrication

Coated cathodes with formulation of active material/carbon black/PVDF = 94/3/3 (wt%) were cut into 60 x 50 mm² size. The electrode was pressed at room temperature with a pressure of 500 kg/cm². Typical thickness of the electrode with the current collector after pressing was 80µm, and the typical active material weight in the disc electrode was 15mg/cm². The electrode was dried at 80°C under a vacuum for 16 hours before cell assembly.

Similar to the cathode, an anode with formulation of MCMB(mesocarbon microbeads)/PVDF = 93/7 (wt%) was cut into 60 x 50 mm². The electrode was pressed at room temperature with an apparent pressure of 500 kg/cm² and dried at 80°C under vacuum for 16 hours before cell assembly. The typical anode active material weight in the disc electrode was 10mg/cm².

The anode and cathode were separated by a glass fiber separator with a rectangular size of 65 x 55 mm². The EC/DMC (1:1) -LiPF₆ 1M (EM Industries) electrolyte was absorbed in the electrodes and separator. The electrodes and separator were compressed between two 70 x 60 mm² glass plates. The whole assembly was put into an Al laminated bag (size approximate 80 x 70 mm²), which was sealed under vacuum. All operations were carried in an Ar filled glove box with water and oxygen level less than 1 ppm.

b) Electrochemical Charging

After measuring the volume of the cell, binder clips

- 28 -

clamped the cell to eliminate electrode shifting in the event of gassing. After rest for 2 hours, it was charged and discharged using C/10 current between 4.2-2.7V once. The cell then was charged to 4.5V with C/10 current, and held at
5 4.5V for 4 hours in an oven set at 60°C. The cell then was removed from the oven and allowed to cool to room temperature before volume measurements were made of the cell assembly.

c) Volume Measurements

10 The volume of the cell before and after charging was measured by immersing the cell in water. The volume is equal to the volume of the displaced water. The volume of gas generated during charging was measured as the volume difference before and after charging. The gas
15 volume then was normalized by the weight of active cathode material.

Comparative Example 1

A LiCoO₂ was purchased from Nippon Chemical and subjected to XRD, electrochemical and gassing tests. The
20 powder was found to be phase pure by XRD (Figure 16). No XRD peak asymmetry was detected. This shows that the LiCoO₂ material does not have a gradient coating. Electrochemical measurements of this powder yielded a specific capacity of 142mAh/g with a cycle efficiency of 95%.
25 This shows that this material has relatively low capacity compared to the invention examples.

Comparative Example 2

- 29 -

A $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ material (N-82) was purchased from Nippon Chemical and subjected to XRD (Figure 17), electrochemical and gassing tests. The powder was found to be phase pure by XRD with lattice parameters of
5 $a=2.8679(2)\text{ \AA}$ and $c=14.699(7)\text{ \AA}$. No peak asymmetry was detected. This shows that the nickel-based material does not have a gradient coating. Electrochemical measurements of this powder yielded a specific capacity of 165mAh/g with a cycle efficiency of 85%, and a gassing
10 volume of 8.6cc/g. This shows that this material has high gassing properties, compared to Example 1.

Comparative Example 3

The two materials in Comparative Examples 1 and 2 were mixed together in a 10/90 ratio (mol%/mol%) and
15 subjected to XRD (Figure 18). The powder was found to have distinct peaks from the two compounds. This shows that asymmetry cannot be obtained just by having two components, which would be the case for a LiCoO_2 coated material where LiCoO_2 is coated as a separate phase onto
20 the core compound.

Comparative Example 4

Synthesis of $\text{Li}_{1.1}\text{Ni}_{0.87}\text{Co}_{0.1}\text{B}_{0.03}\text{O}_2$

19.56g LiNO_3 , 20.81g Ni(OH)_2 , 2.40g Co(OH)_2 and 0.27g B_2O_3 were placed in a Retsch/Brinkmann mortar
25 grinder (model RM100) fitted with agate mortar and pestle and ground for 5 minutes. The resultant homogeneous powder was placed in an alumina combustion tray, and

- 30 -

sintered in a Degussa-Ney muffle furnace (model 3-1750), under the following profile: ramp 5°C/minute to 450°C, hold at 450°C for 4 hours, ramp 2°C/minute to 750°C, hold at 750°C for 4 hours. The sample was allowed to cool

5 naturally to room temperature and then ground 5 minutes in the mortar grinder to attain a particle size range of 1-50µm. When subjected to XRD this material was shown to have no gradient profile. No impurities were visible (Figure 19). The lattice parameters were $a=2.8743(5)$, $c=14.183(2)$.

10 Electrochemical measurements of this powder yielded a specific capacity of 174mAh/g with a cycle efficiency of 85%, and a gassing volume of 18.0cc/g. This shows that this material has bad gassing properties, but an acceptably high capacity compared to Example 3.

15 Example 6

Synthesis of $\text{LiMg}_{0.01}\text{Ni}_{0.87}\text{Co}_{0.08}\text{Mn}_{0.05}\text{O}_2$ Base Material

73.83g LiNO_3 (excess Lithium was used), 0.59g $\text{Mg}(\text{OH})_2$, 29.69g $\text{Co}(\text{OH})_2$ and 5.86g MnCO_3 were mixed 5 minutes in a Retsch/Brinkmann mortar grinder (model 20 RM100) fitted with an agate mortar and pestle. The mixed materials were added to a 1L high density polyethylene jar containing 82.25g $\text{Ni}(\text{OH})_2$ and mixed by shaking. The homogeneous precursor powders were placed in an alumina crucible, and sintered under air using the following heating 25 profile: ramp 5°C/minute to 450°C, hold at 450°C for 4 hours, ramp 2°C/minute to 775°C, and hold for 24 hours. The sample was then allowed to cool naturally to room

- 31 -

temperature and ground for 5 minutes to break up agglomerates. When subjected to XRD this material was shown to be the phase pure rhombohedral structure of type α - NaFeO_2 with no detectable impurities.

5 Example 7

Synthesis of 1% (mol/mol) LiCoO_2 gradient having a $\text{LiMg}_{0.01}\text{Ni}_{0.87}\text{Co}_{0.08}\text{Mn}_{0.05}\text{O}_2$ base.

0.706g LiNO_3 , and 2.97g $\text{Co}((\text{NO})_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 150ml distilled H_2O to which 100g base material
10 (described above Example 6) was added. The H_2O was evaporated off on a hot plate during stirring. The obtained dried cake was ground for 5 minutes in the mortar grinder, placed in an alumina crucible, and sintered under air using the following heating profile: ramp $5^\circ\text{C}/\text{minute}$ to 450°C ,
15 hold at 450°C for 1hour, ramp $2^\circ\text{C}/\text{minute}$ to 750°C , and hold for 2 hour. The sample was then allowed to cool naturally to room temperature and ground for 5 minutes to break up agglomerates. When subjected to XRD this material was shown to have a gradient profile. No other
20 phase was visible by means of XRD.

Example 8

Synthesis of 2.5% (mol/mol) LiCoO_2 gradient having a $\text{LiMg}_{0.01}\text{Ni}_{0.87}\text{Co}_{0.08}\text{Mn}_{0.05}\text{O}_2$ base.

The experimental procedure was similar to the
25 procedure described in Example 7, but 1.76g LiNO_3 , and 7.42g $\text{Co}((\text{NO})_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 150ml distilled H_2O . When subjected to XRD this material was shown to have a

- 32 -

gradient profile. No other phase was visible by means of XRD.

Example 9

Synthesis of 5% (mol/mol) LiCoO_2 gradient having a

5 $\text{LiMg}_{0.01}\text{Ni}_{0.87}\text{Co}_{0.08}\text{Mn}_{0.05}\text{O}_2$ base.

The experimental procedure was similar to the procedure described in Example 7, but 3.53g LiNO_3 , and 14.85g $\text{Co}((\text{NO})_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 150 ml distilled H_2O . When subjected to XRD this material was shown to
10 have a gradient profile. No other phase was visible by means of XRD.

Example 10

Synthesis of 10% (mol/mol) LiCoO_2 gradient having a

$\text{LiMg}_{0.01}\text{Ni}_{0.87}\text{Co}_{0.08}\text{Mn}_{0.05}\text{O}_2$ base.

15 The experimental procedure was similar to the procedure described in Example 7, but 7.06g LiNO_3 , and 29.69g $\text{Co}((\text{NO})_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 150ml distilled H_2O . When subjected to XRD this material was shown to have a gradient profile. No other phase was visible by
20 means of XRD.

Example 11

Synthesis of 10% (mol/mol) LiCoO_2 gradient having a

$\text{LiMg}_{0.01}\text{Ni}_{0.87}\text{Co}_{0.08}\text{Mn}_{0.05}\text{O}_2$ base.

The experimental procedure was similar to the
25 procedure described in Example 10, but a higher heating temperature of 800°C was used instead of 750°C .

Example 12

- 33 -

Synthesis of $\text{LiMg}_{0.03}\text{Ni}_{0.87}\text{Co}_{0.10}\text{Mn}_{0.03}\text{O}_2$ - Base Material

74.7g LiNO_3 (excess Lithium was used), 1.77g $\text{Mg}(\text{OH})_2$, 8.13g Co_3O_4 , and 3.49g MnCO_3 were mixed 5 minutes in a Retsch/Brinkmann mortar grinder (model RM100) fitted with an agate mortar and pestle. The mixed materials were added to a 1L high density polyethylene jar containing 65.79g NiO and mixed by shaking. The homogeneously mixed precursor powders were placed in an alumina crucible, and sintered under air using the following heating profile: ramp $5^\circ\text{C}/\text{minute}$ to 450°C , hold at 450°C for 4 hours, ramp $2^\circ\text{C}/\text{minute}$ to 850°C , and hold for 6 hours. The sample was then allowed to cool naturally to room temperature and ground for 5 minutes to break up agglomerates. A second calcination procedure, using the same heating profile as the first calcination, was then applied. When subjected to XRD this material was shown to contain the phase pure rhombohedral structure with no other detectable impurities.

Example 13

Synthesis of 5% (mol/mol) LiCoO_2 gradient having a $\text{LiMg}_{0.03}\text{Ni}_{0.87}\text{Co}_{0.10}\text{Mn}_{0.03}\text{O}_2$ base.

The experimental procedure was similar to the procedure described in Example 7, but 3.53g LiNO_3 , and 14.85g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 150ml distilled H_2O , and a higher temperature of 800°C was used instead of 750°C . When subjected to XRD this material was shown to have a gradient profile. No other phase was visible by

- 34 -

means of XRD. Base material used was from Example 12.

Example 14

Synthesis of 10% (mol/mol) LiCoO_2 gradient having a $\text{LiMg}_{0.03}\text{Ni}_{0.87}\text{Co}_{0.10}\text{Mn}_{0.03}\text{O}_2$ base.

5 The experimental procedure was similar to the procedure described in Example 13, but 7.06g LiNO_3 , and 29.69g $\text{Co}((\text{NO})_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 150ml distilled H_2O . When subjected to XRD this material was shown to have a gradient profile. No other phase was visible by
10 means of XRD.

Example 15

Synthesis of $\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ Base Material

77.27g LiNO_3 (excess Lithium was used), 4.74g $\text{Co}(\text{OH})_2$, and 5.86g MnCO_3 were mixed 5 minutes in a
15 Retsch/Brinkmann mortar grinder (model RM100) fitted with an agate mortar and pestle. The mixed materials were added to a 1L high density polyethylene jar containing 85.02g $\text{Ni}(\text{OH})_2$ and mixed by shaking. The homogeneous precursor powders were placed in an alumina crucible, and
20 sintered under air using the following heating profile: ramp $5^\circ\text{C}/\text{minute}$ to 450°C , hold at 450°C for 4 hours, ramp $2^\circ\text{C}/\text{minute}$ to 775°C , and hold for 24 hours. The sample was then allowed to cool naturally to room temperature and ground for 5 minutes to break up agglomerates. When
25 subjected to XRD this material was shown to be phase pure with no visible impurities.

Example 16

- 35 -

Synthesis of $\text{LiNi}_{0.87}\text{Co}_{0.1}\text{B}_{0.03}\text{O}_2$ Base Material

19.56g LiNO_3 (excess Lithium was used), 20.81g $\text{Ni}(\text{OH})_2$, 2.40g $\text{Co}(\text{OH})_2$ and 0.27g B_2O_3 were placed in a Retsch/Brinkmann mortar grinder (model RM100) fitted with agate mortar and pestle and ground for 5 minutes. The resultant homogeneous powder was placed in an alumina combustion tray, and sintered in a Degussa-Ney muffle furnace (model 3-1750), under air using the following profile: ramp $5^\circ\text{C}/\text{minute}$ to 450°C , hold at 450°C for 4 hours, ramp $2^\circ\text{C}/\text{minute}$ to 750°C , hold at 750°C for 4 hours. The sample was allowed to cool naturally to room temperature and then ground 5 minutes in the mortar grinder to attain a particle size range of 1-50 μm . When subjected to XRD this material was shown to be phase pure with no visible impurities.

Example 17

XRD Analysis

Powder X-ray diffraction patterns were collected for Example 6, 7, 8, 9, 10, 13, 14 and 15 in a continuous scan between 5 and 120 degrees in 2-theta (θ) using an automated Shimadzu XRD-6000 diffractometer. The gradient coating was detected by studying the increasing degree of asymmetry in the Bragg reflections. In particular the (104) peak at about 44.4 degrees in 2-theta was used, Figure 20. Figure 20 shows how the asymmetry of (104) is continuously increased with the amount LiCoO_2 used. The respective XRD patterns in Figure 20 have been adjusted for

- 36 -

2-theta zero point position and normalized in intensity in order to easily compare the patterns. a= Example 6 (Base Compound), b= Example 7 (1%LiCoO₂), c= Example 8 (2.5%LiCoO₂), d= Example 9 (5%LiCoO₂), e= Example 10 (10%LiCoO₂).

Example 18

Atom structure Analysis Using Rietveld Technique

The X-ray diffractograms from Example 17 were subjected to atom structure analysis using the Rietveld technique as implemented in the Fullprof program (Ref. Fullprof - Version 3.5d Oct98-LLB-JRC, Author: Juan Rodriguez-Carvajal, Laboratoire Leon Brillouin (CEA-CNRS), France). Procedures for atom structure refinements are evident to those skilled in the art. Using these refinements the relative amounts of Ni²⁺ ions occupying the Li-site were refined. In addition the relative occupation of oxygen in the oxygen site was refined for each diffractogram obtained from sample patterns in Example 14. The occupation of Mg²⁺ ions in the Li site and Co- and Mn-ions occupying the Ni site were treated as constants, as expressed by the chemical formula (Li_{1-x}Mg_{0.01}Ni_x)(Ni_{0.87-x}Li_xCo_{0.08}Mn_{0.05})O_z. Oxygen occupation z was refined as an individual parameter, while the occupation of Li and Ni could vary between the two respective sites, i.e. the Ni occupation was coupled to the Li occupation in one single parameter, x, so that intermixing between sites was allowed. This procedure allows the determination of the amount nickel ions that are disordered

- 37 -

into the Li site during synthesis. Figures 21 and 22 show that first cycle efficiency is increased as nickel disorder ($\%Ni^{2+}$) is decreasing and relative oxygen levels z are increased. This shows that as order/disorder properties are improved efficiency and capacity of the material will increase.

Example 19

Synthesis of 5% (mol/mol) $LiCoO_2$ gradient having a $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$ base.

10 The experimental procedure used was similar to the procedure of Example 9, but the base material used was $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$ from Example 15.

Example 20

Synthesis of 5% (mol/mol) $LiCoO_2$ gradient having a $LiNi_{0.87}Co_{0.10}B_{0.03}O_2$ base.

15 The experimental procedure used was similar to the procedure of Example 9, but the base material used was $LiNi_{0.87}Co_{0.10}B_{0.03}O_2$ from Example 16.

Example 21

20 Samples from Examples 6, 9, 15, 16, 19 and 20 were subjected to electrochemical testing. Figure 23 is a plot of relative capacity retention for the three base compounds (Examples 6, 15 and 16). Figure 24 shows relative capacity retention for the 5% $LiCoO_2$ coated compounds, with an obtained gradient profile from calcination (Examples 9, 19 and 20). This shows that $Li_{1.05}Mg_{0.01}Ni_{0.82}Co_{0.08}Mn_{0.05}O_2$ has the overall best capacity

25

- 38 -

retention, which is a preferred embodiment.

While this invention has been particularly shown
and described with references to preferred embodiments
thereof, it will be understood by those skilled in the art that
5 various changes in form and details may be made therein
without departing from the scope of the invention
encompassed by the appended claims.

[RELATED APPLICATION]

This application claims the benefit of U.S.
10 Provisional Application No.60/298,791 and 60/298,798,
both of which were filed on June 15, 2001, and also the
benefit of U.S. Patent Application No. 10/073,674 filed on
February 11, 2002. The entire teachings of the three
applications are incorporated herein by reference.

15 [INDUSTRIAL APPLICABILITY]

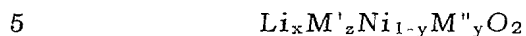
As described above, according to the invention,
there are provided a composition suitable for employment in
a cathode of a lithium battery, a method of forming the
composition, and a lithium battery employing the
20 composition as a cathode material.

- 39 -

CLAIMS

1. A composition, comprising:

a) a core having an empirical formula



wherein: x is greater than about 0.1 and equal to or less than about 1.3,

y is greater than about 0.0 and equal to or less than about 0.5,

10 z is greater than 0.0 and equal to or less than about 0.2,

M' is at least one member of the group consisting of sodium, potassium, calcium, magnesium and strontium, and

15 M'' is at least one member of the group consisting of cobalt, iron, manganese, chromium, vanadium, titanium, magnesium, silicon, boron, aluminum and gallium: and
b) a coating on the core having a greater ratio of cobalt to nickel than the core

20

2. The composition of Claim 1, wherein M'' includes cobalt.

3. The composition of Claim 2, wherein y is in a range
25 of between about 0.1 and about 0.5.

4. The composition of Claim 3, wherein y is about 0.1.

- 40 -

5. The composition of Claim 3, wherein y is about 0.2

6. The composition of Claim 2, wherein M' includes
5 magnesium

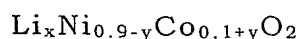
7. The composition of Claim 6, wherein M" further
includes boron.

10 8. The composition of Claim 6, wherein M" further
includes manganese.

9. The composition of Claim 6, wherein the sum of x
and z equals about one.
15

10. The composition of Claim 1, wherein the ratio of
cobalt to nickel increases as a gradient from the core to an
outer surface of the coating.

20 11. The composition of Claim 1, wherein the core has
an empirical formula

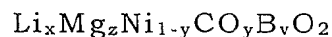


wherein: x is greater than about 0.1 and equal to or less
than 1.3, and

25 y is greater than zero and equal to or less than
about 0.4.

- 41 -

12. The composition of Claim 1, wherein the core has an empirical formula



wherein: y is greater than 0.0 and equal to or less than
5 about 0.4,

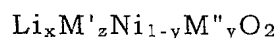
v is greater than about 0.0 and equal to or less than about 0.4, and

B is at least one member of the group consisting of manganese, boron, aluminum and gallium.

10

13. A method of forming a composition, comprising the steps:

a) drying a water solution of LiNO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in which a core material is immersed, said core material having
15 an empirical formula



wherein: x is greater than about 0.1 and equal to or less than about 1.3,

y is greater than about 0.0 and equal to or less
20 than about 0.5,

z is greater than about 0.0 and equal to or less than about 0.2,

M' is at least one member of the group consisting of sodium, potassium, nickel, calcium, magnesium and
25 strontium, and

M'' is at least one member of the group consisting of cobalt, iron, manganese, chromium, vanadium, titanium,

- 42 -

magnesium, silicon, boron, aluminum and gallium, to thereby form a precursor coating on said core material; and b) calcining the precursor coating, thereby forming the composition.

5

14. The method of Claim 13, wherein the stoichiometric ratio of LiNO_3 to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is in a range of between about 0.0 and about 1.2.

10

15. The method of Claim 14, wherein the precursor coating is calcined by heating the coating to a temperature in a range of between about 500 and about 900°C for a period of time in a range of between about 0.2 and about 12 hours.

15

16. The method of Claim 15, wherein the precursor coating is calcined by heating the coating and the core material at a rate in a range of between about 5°C and about 100°C per minute to a temperature in a range of between about 300°C and about 500°C, which temperature then is maintained for a period of time in a range of between about 0.2 hours and about 4 hours, and then heating the precursor coating and the core material at a rate of between about 5°C and about 50°C per minute to a temperature of between about 600°C and about 900°C, at which temperature the coating is maintained for a period of time in a range of between about 0.2 and about 12 hours.

25

- 43 -

17. The method of Claim 13, wherein the core material includes $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

5 18. The method of Claim 13, wherein the core material includes $\text{Li}_{1.1}\text{Ni}_{0.87}\text{Co}_{0.1}\text{B}_{0.03}\text{O}_2$.

19. The method of Claim 13, where the core material includes $\text{Li}_{1.07}\text{Mg}_{0.03}\text{Ni}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$.

10

20. The method of Claim 13, wherein the amount of coating formed on the core material is greater than 0.0 mole percent and equal to or less than about 15.0 mole percent of the composition.

15

21. The method of Claim 13, wherein the amount of coating formed on the core material is greater than 5.0 mole percent and equal to or less than about 15.0 mole percent of the composition.

20

22. The method of Claim 13, wherein the amount of coating formed on the core material is greater than 5.0 mole percent and equal to or less than about 10.0 mole percent of the composition.

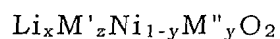
25

23. A lithium battery having a cathode that includes a composition, said composition including particles,

- 44 -

comprising:

a) a core having an empirical formula



wherein: x is greater than about 0.1 and equal to or less

5 than about 1.3,

y is greater than about 0.0 and equal to or less
than about 0.5,

z is equal to or greater than about 0.0 and equal to
or less than about 0.2,

10 M' is at least one member of the group consisting of
sodium, potassium, nickel, calcium, magnesium and
strontium, and

M'' is at least one member of the group consisting
of cobalt, iron, manganese, chromium, vanadium, titanium,
15 magnesium, silicon, boron, aluminum and gallium; and

b) a coating having a greater ratio of cobalt to nickel than
the core.

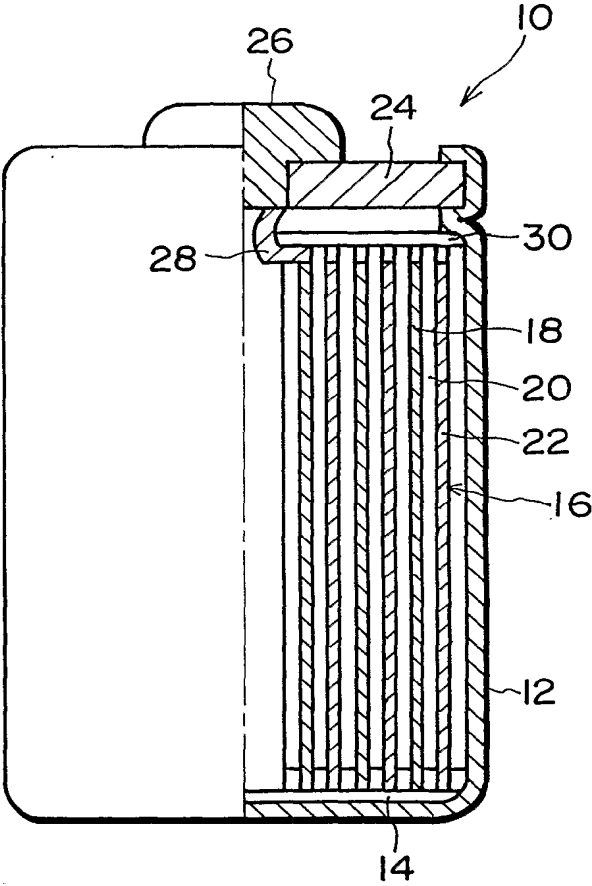


FIG. 1

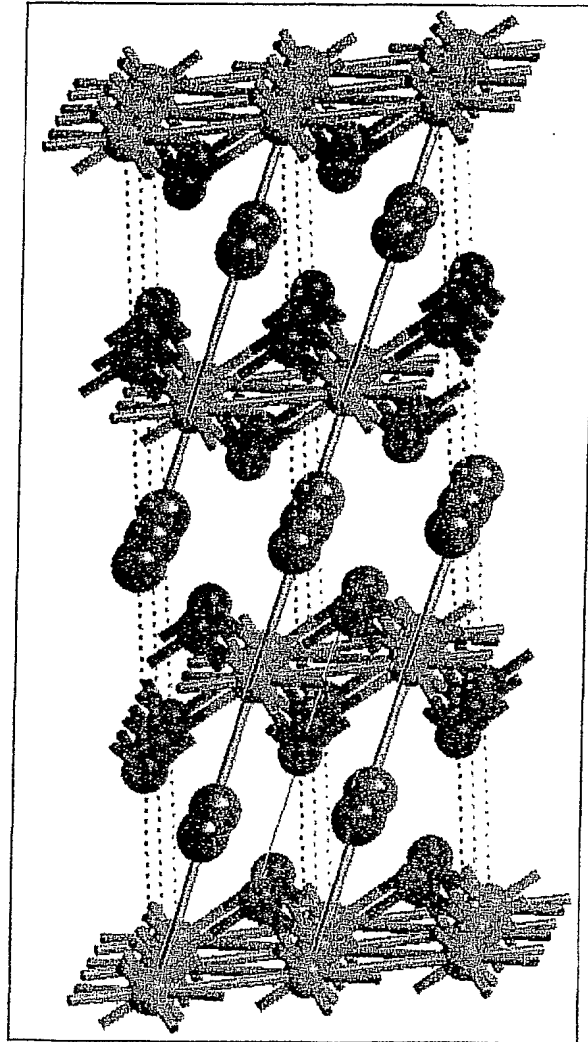
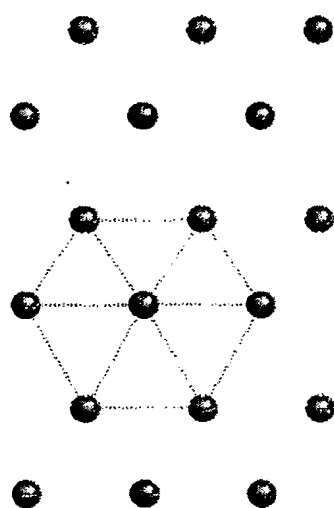
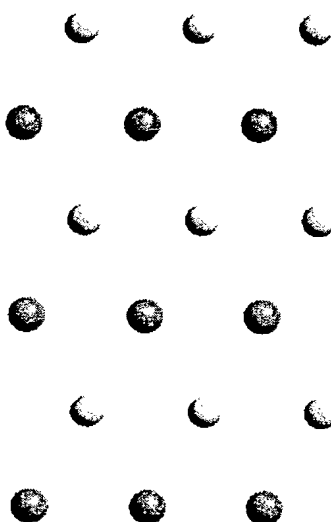


FIG. 2

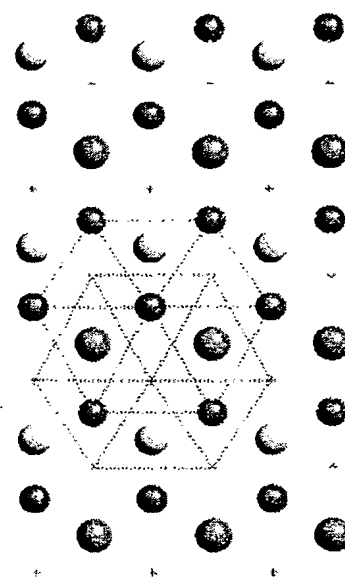
3/24



(A)



(B)



(C)

FIG. 3

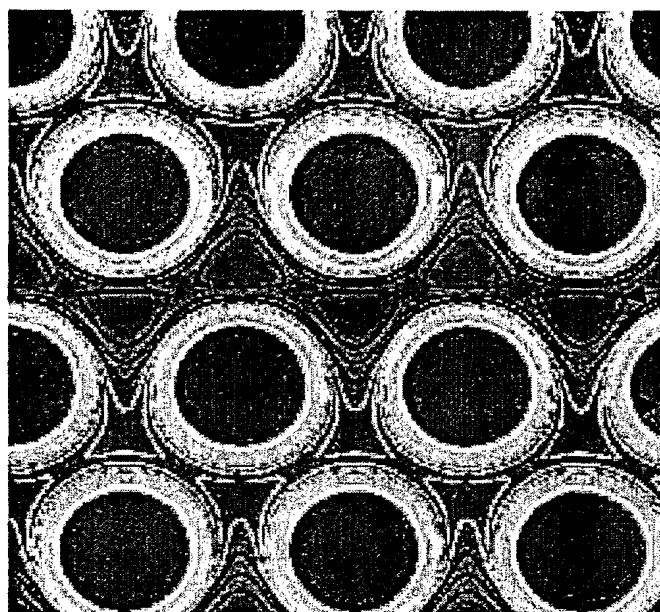
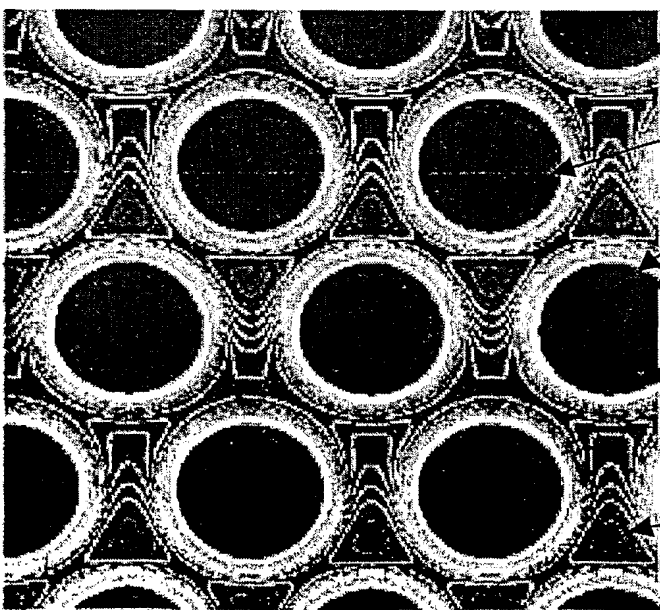


Figure 4a

low charge density



high charge density

low charge density

Figure 4b

FIG. 4

5/24

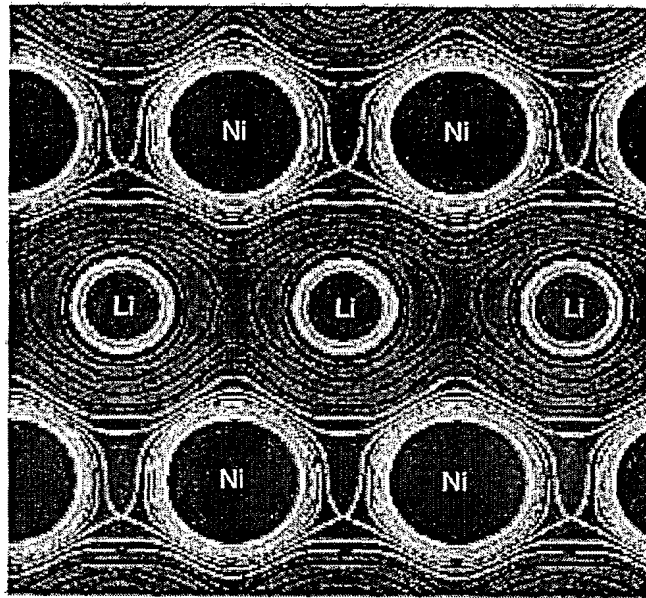


FIG. 5

6/24

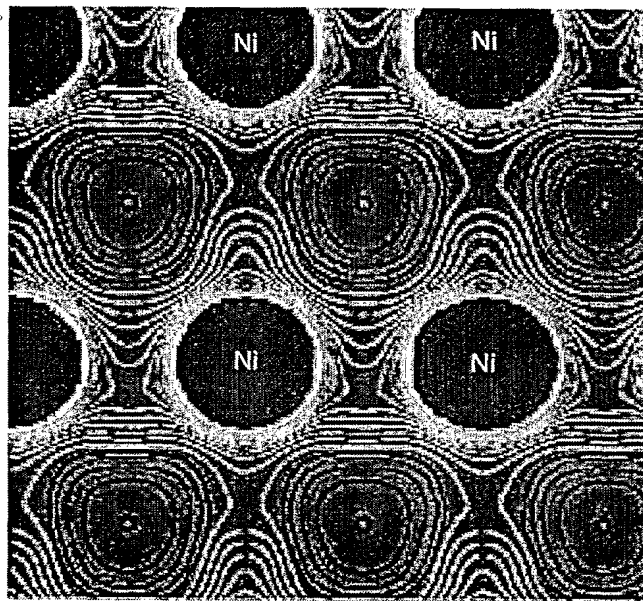


FIG. 6

7/24

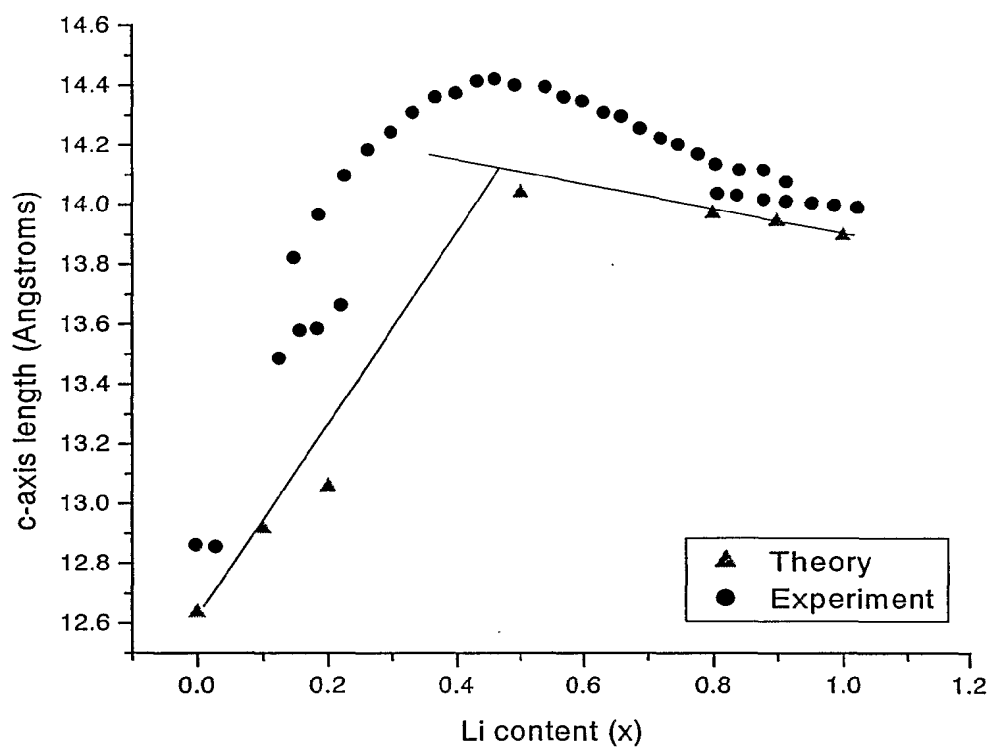


FIG. 7

8/24

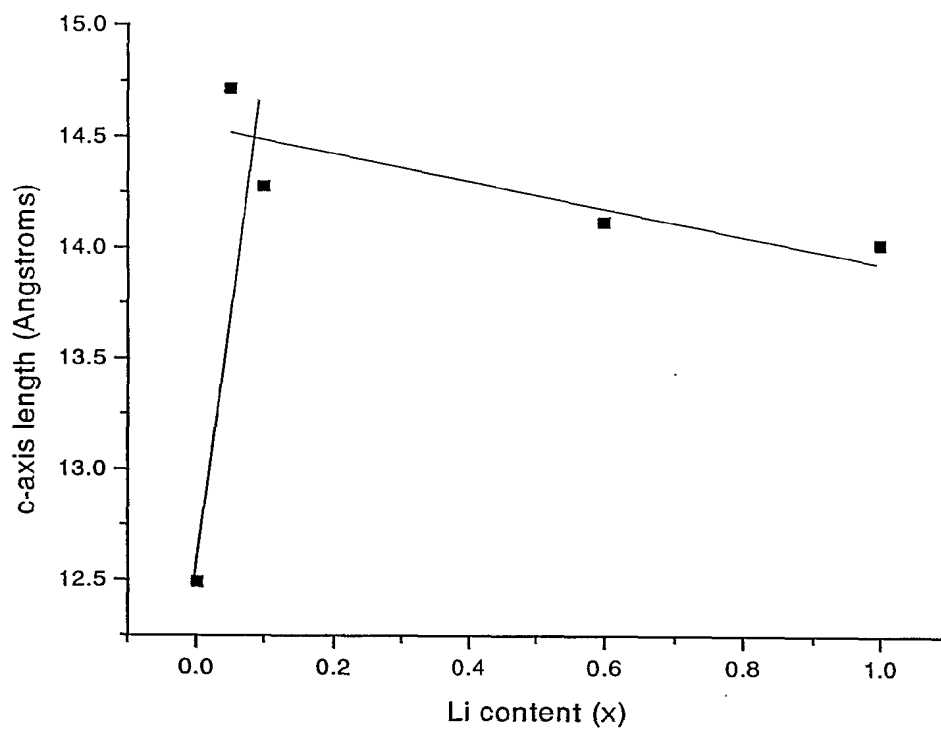


FIG. 8

9/24

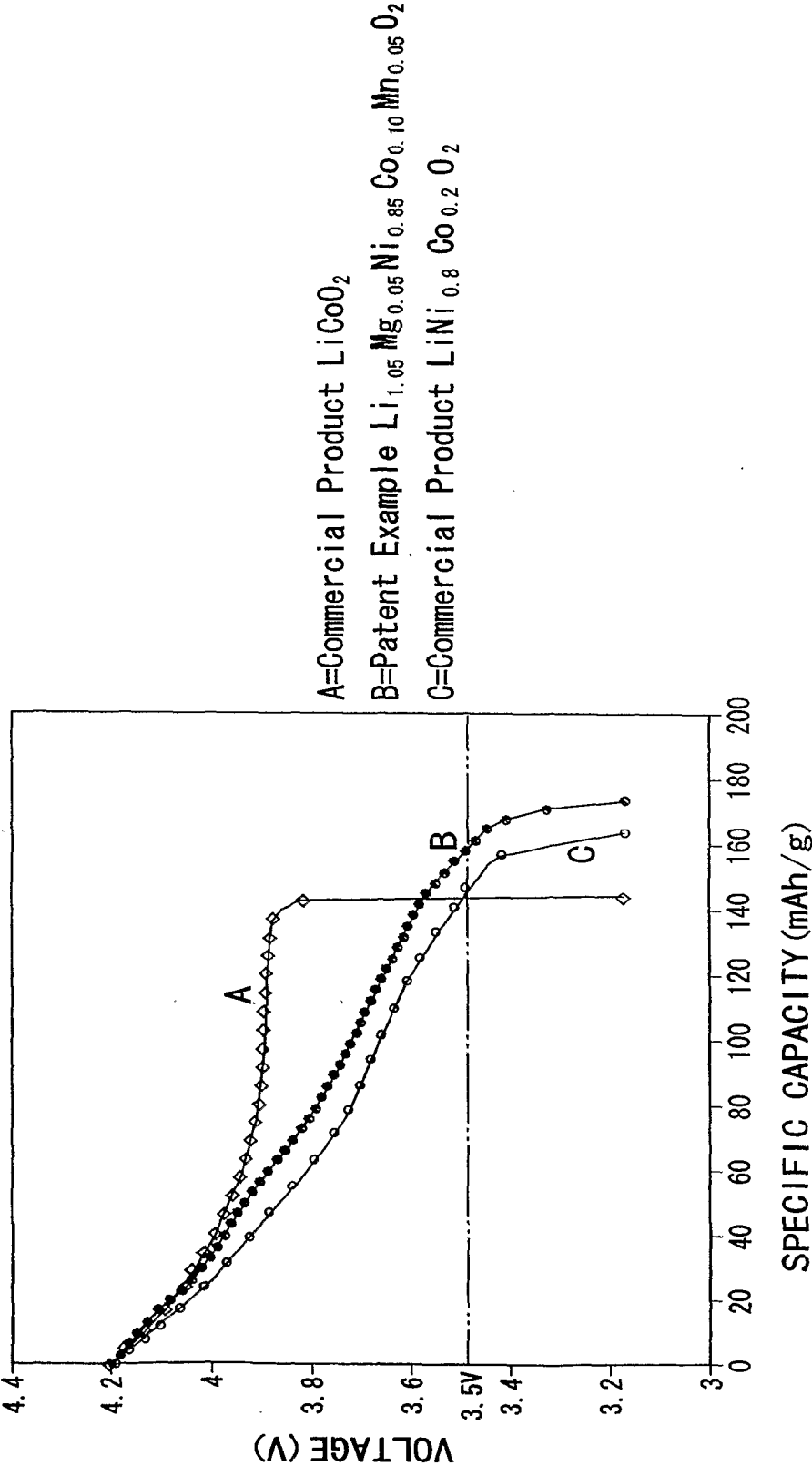
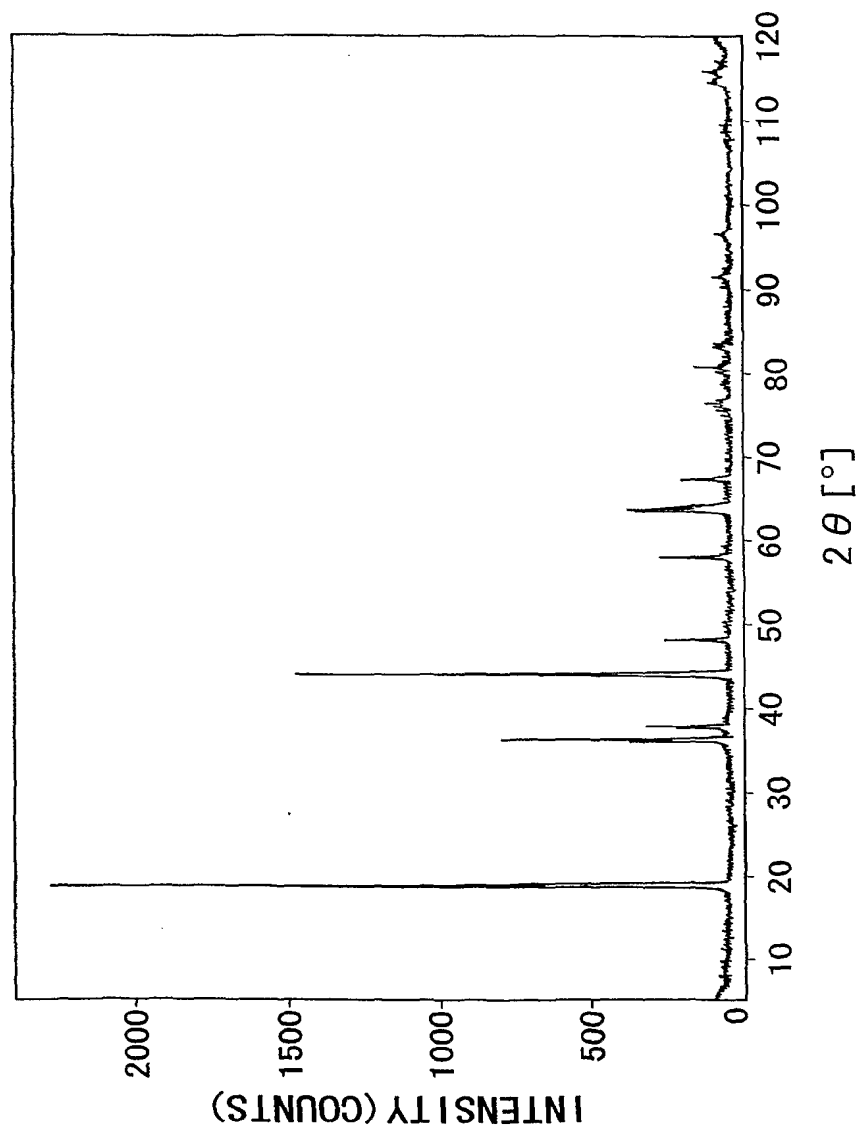
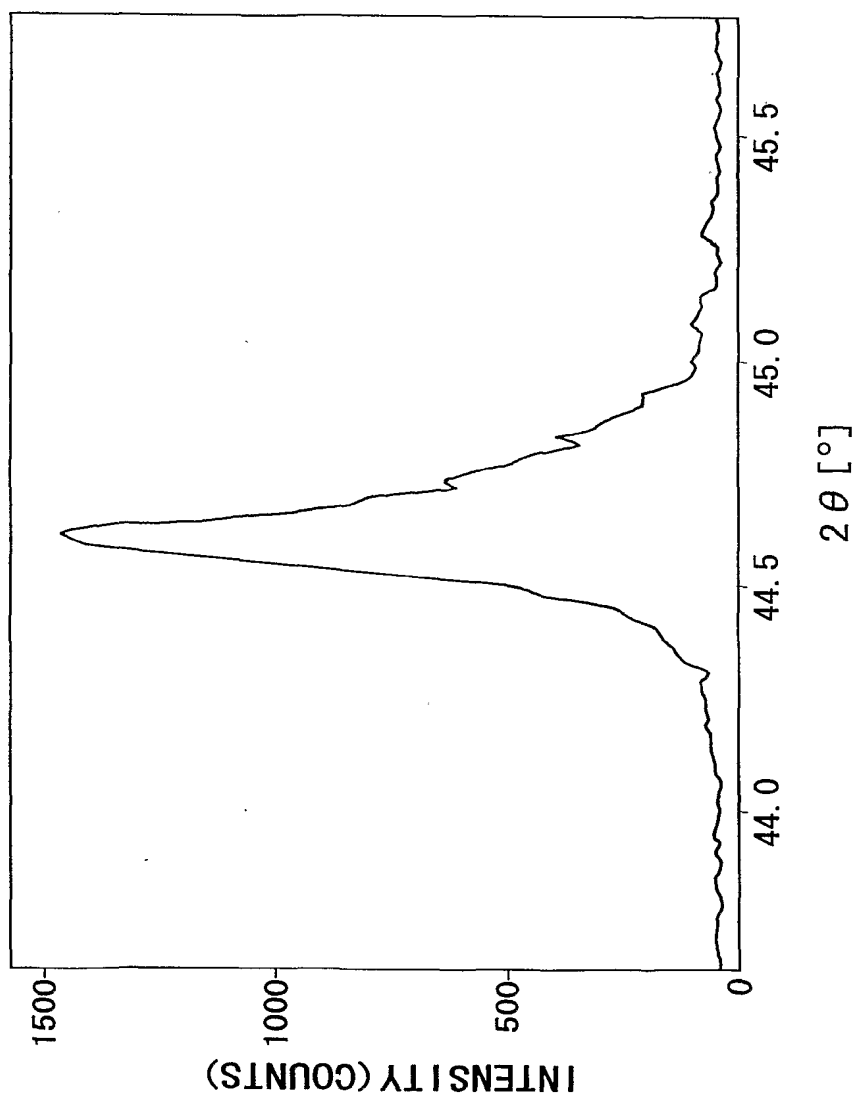


FIG. 9

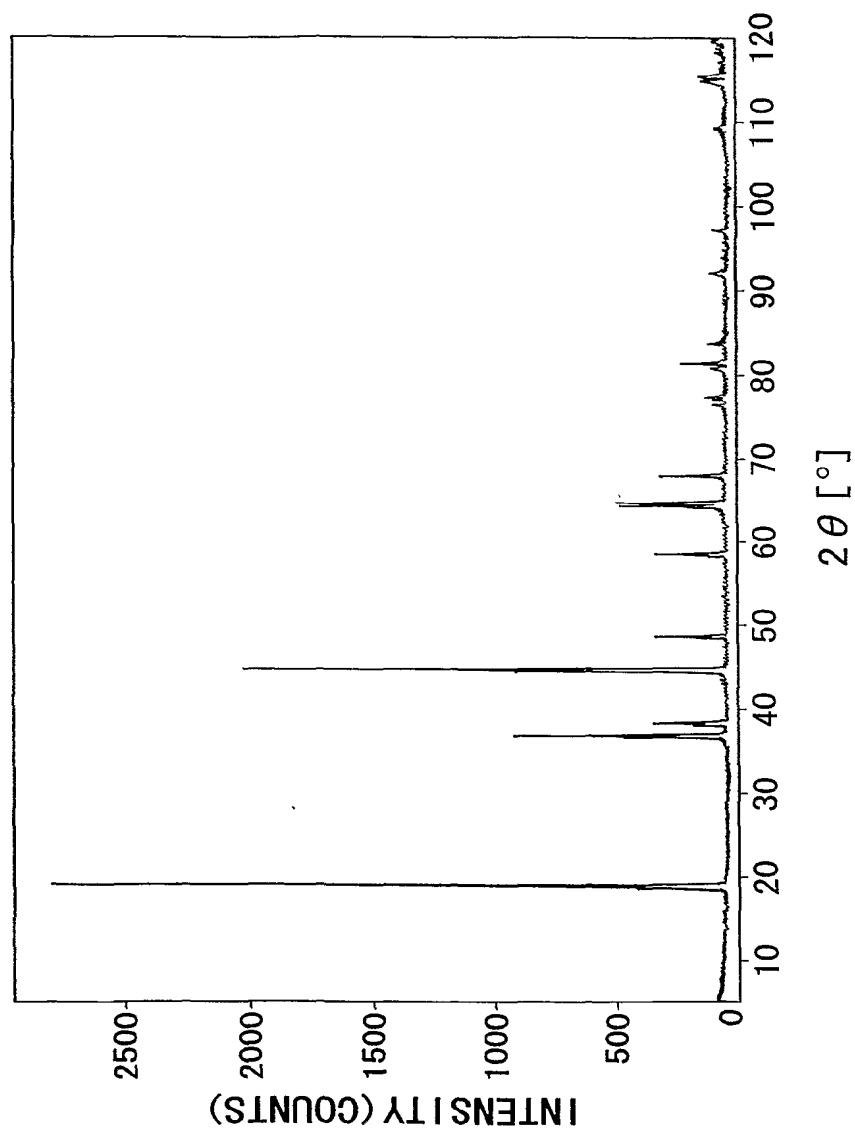
10/24

**FIG. 10**

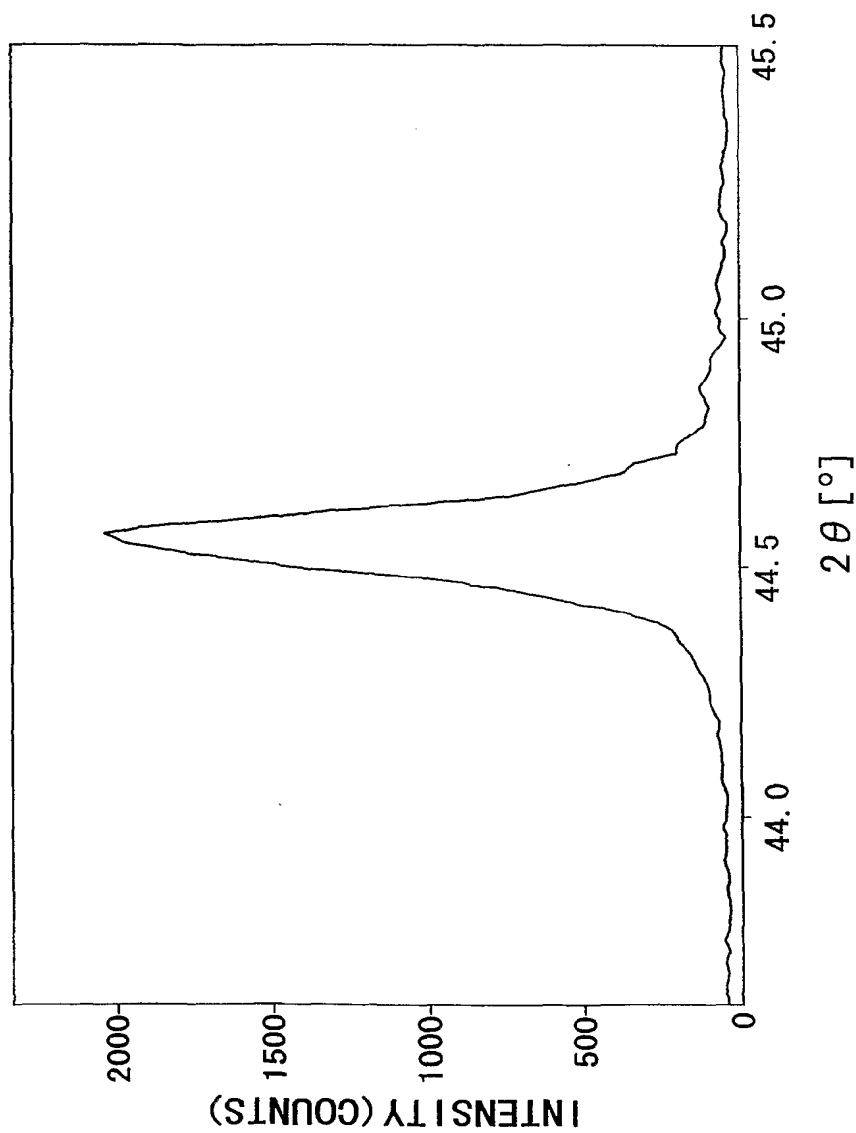
11/24

**FIG. 11**

12/24

**FIG. 12**

13/24

**FIG. 13**

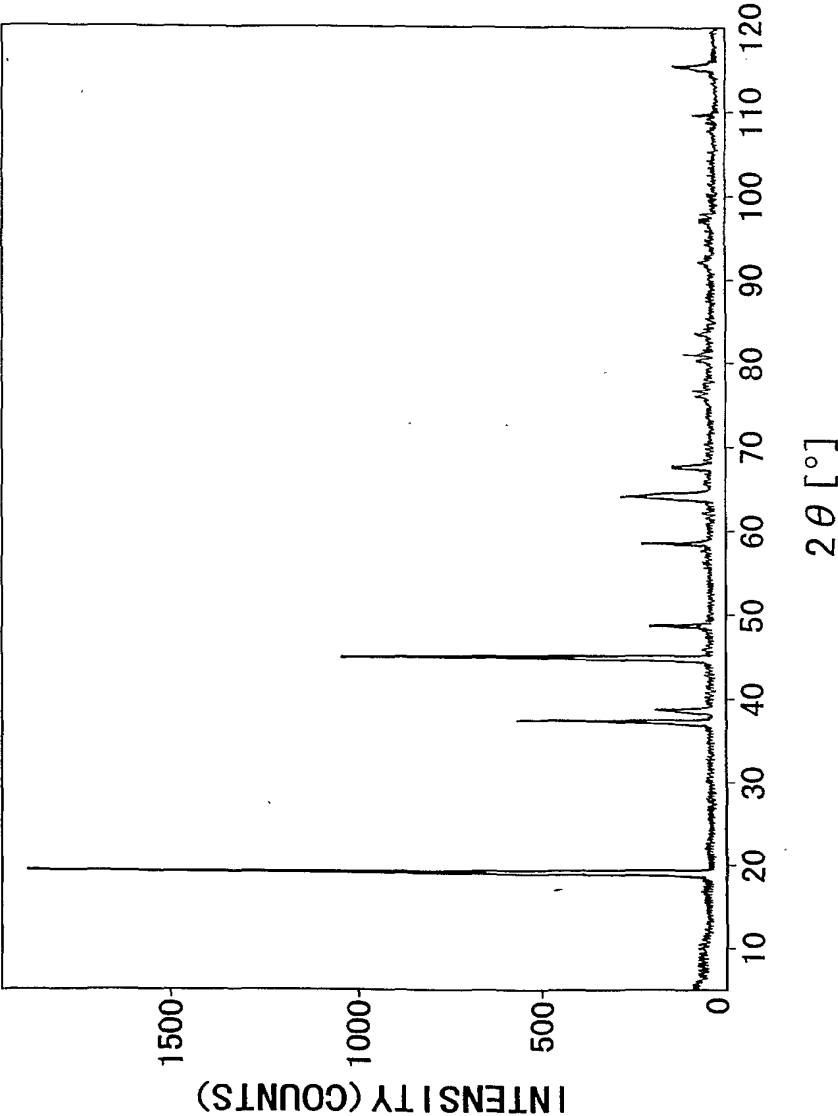
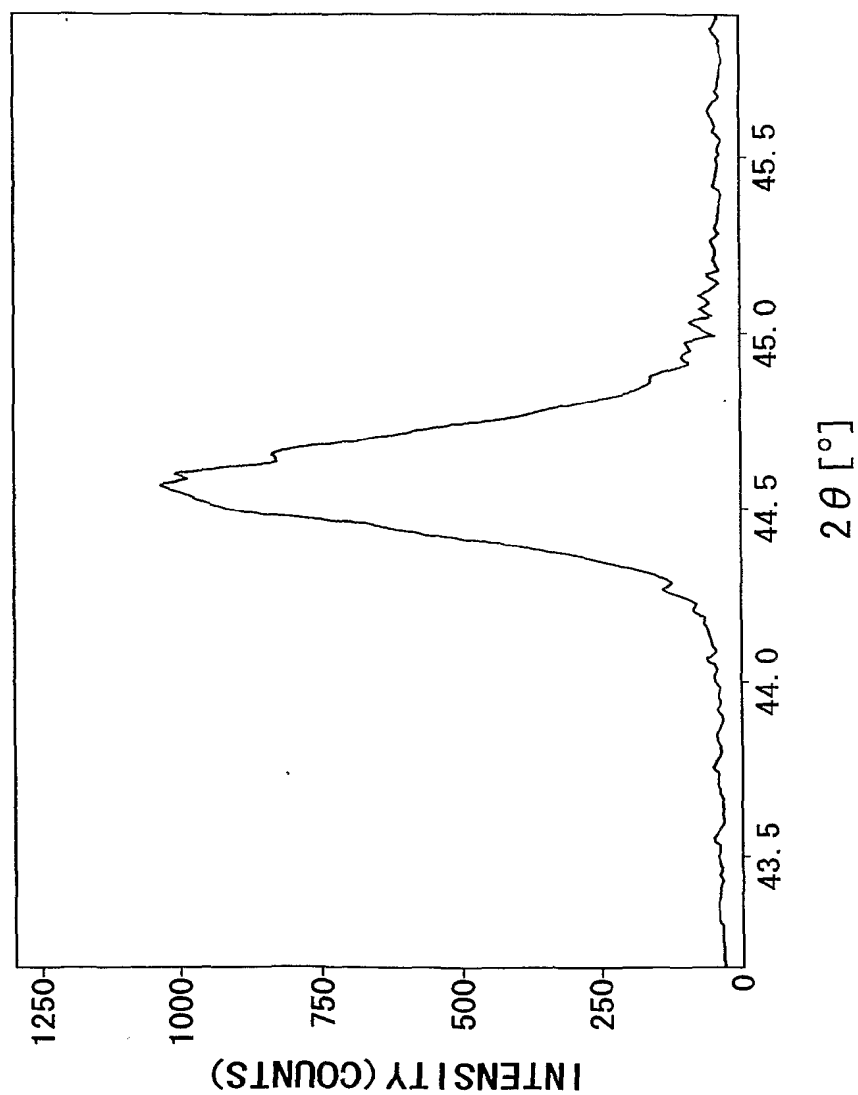


FIG. 14

15/24

**FIG. 15**

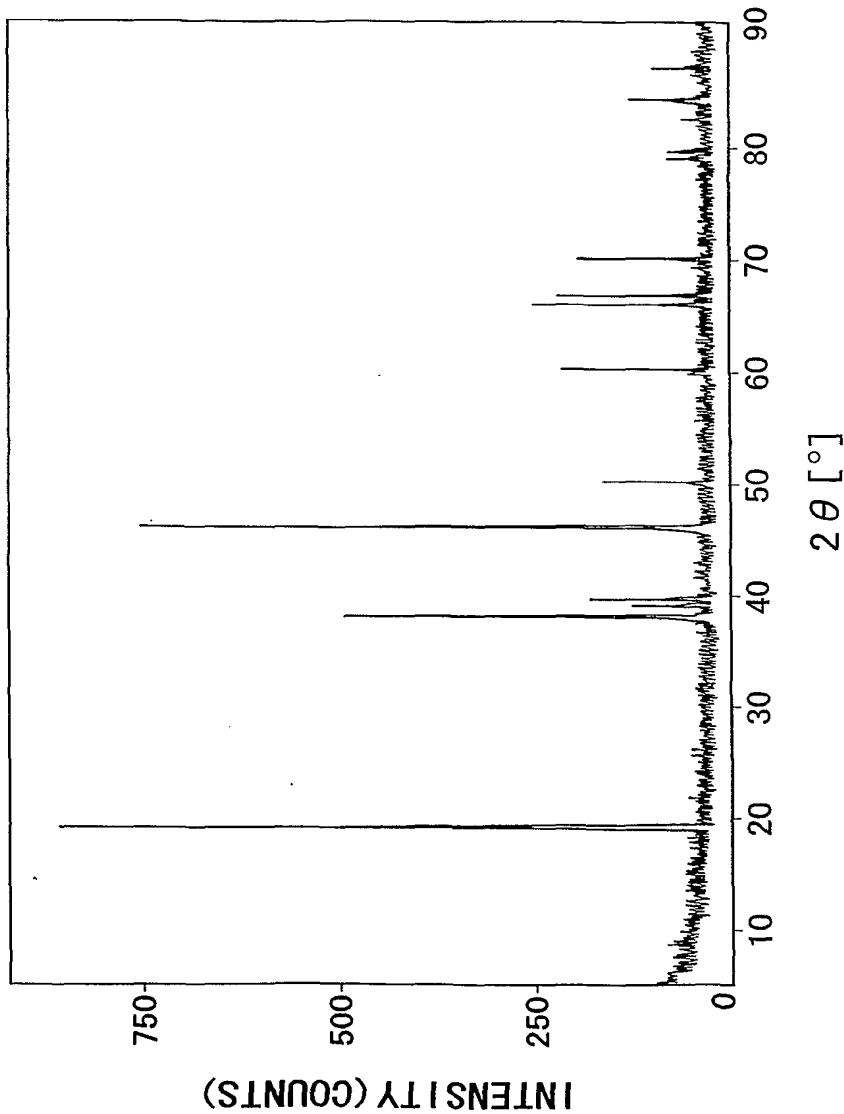
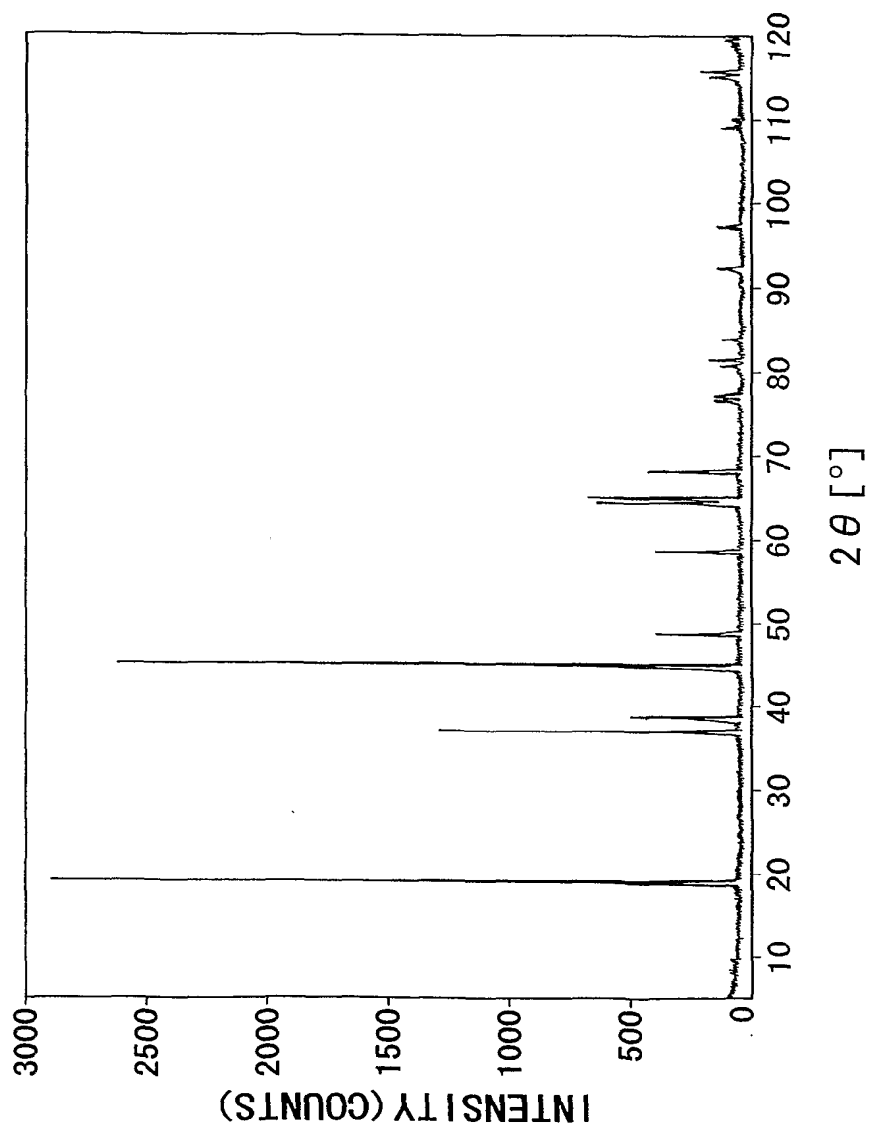
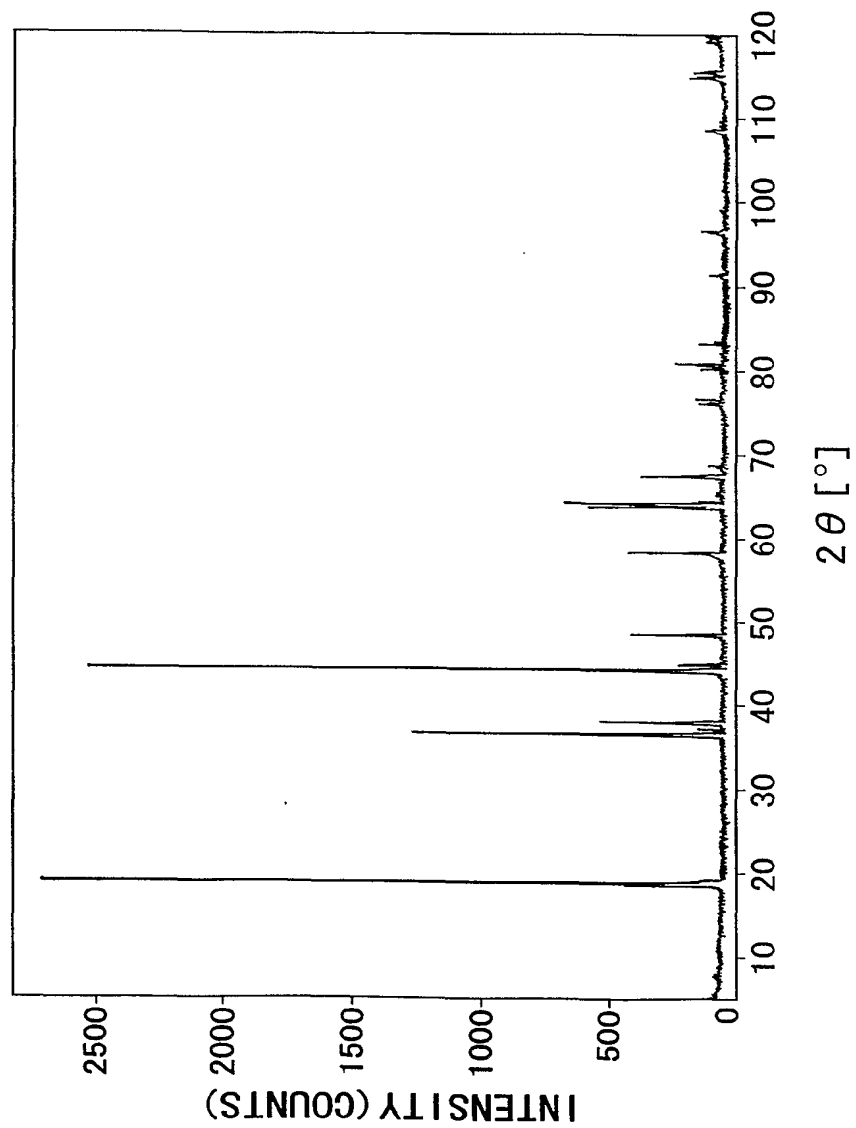


FIG. 16

17/24

**FIG. 17**

18/24

**FIG. 18**

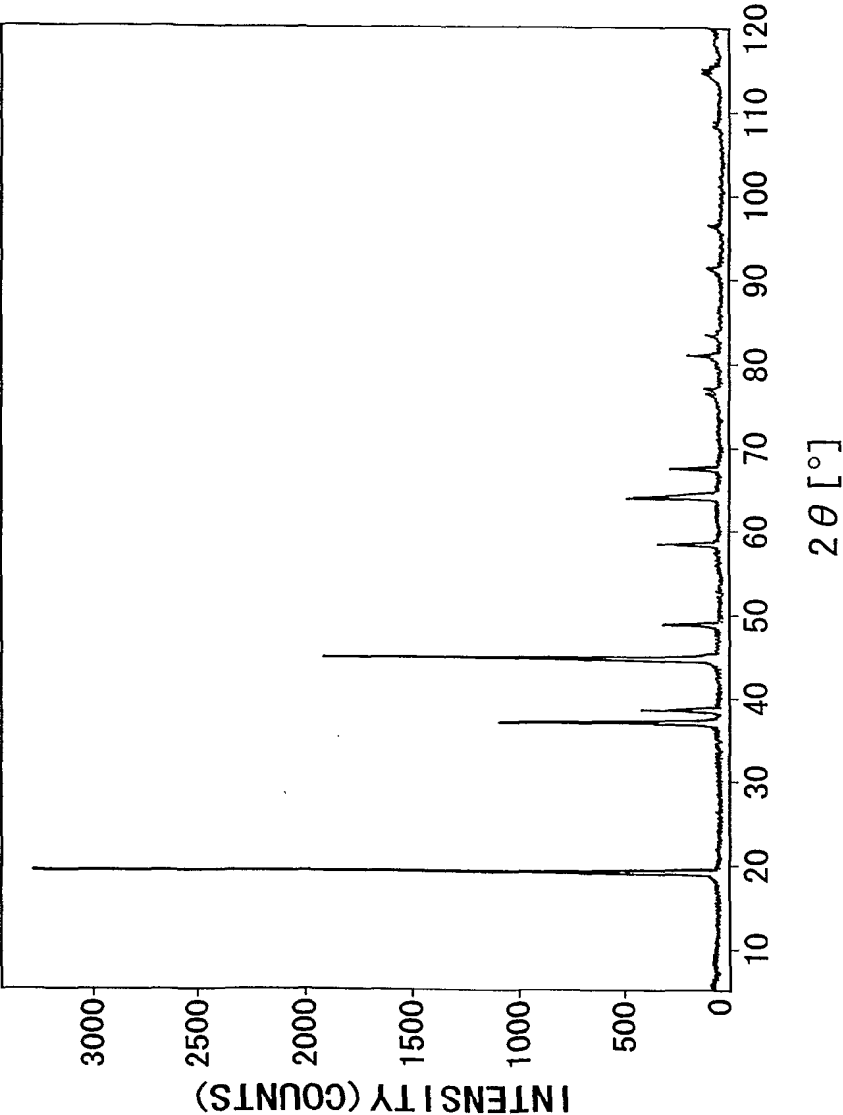
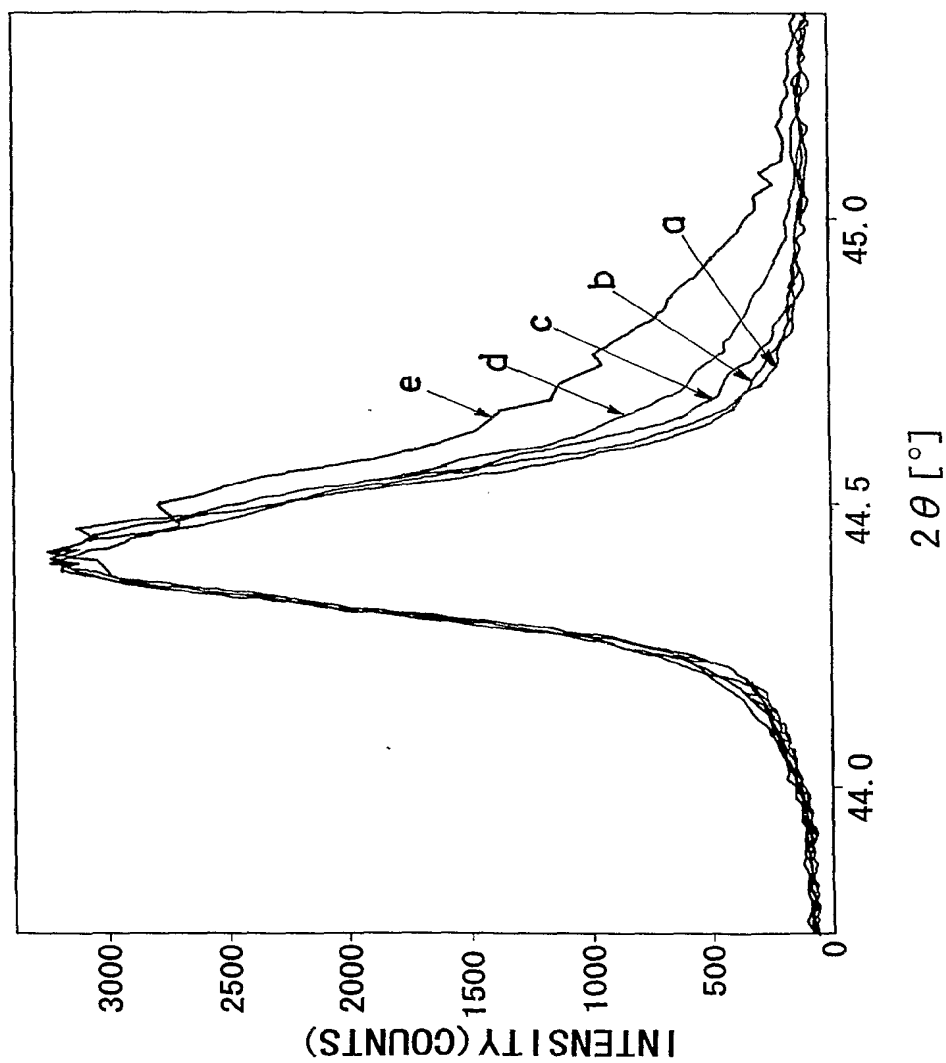


FIG. 19

20/24

**FIG. 20**

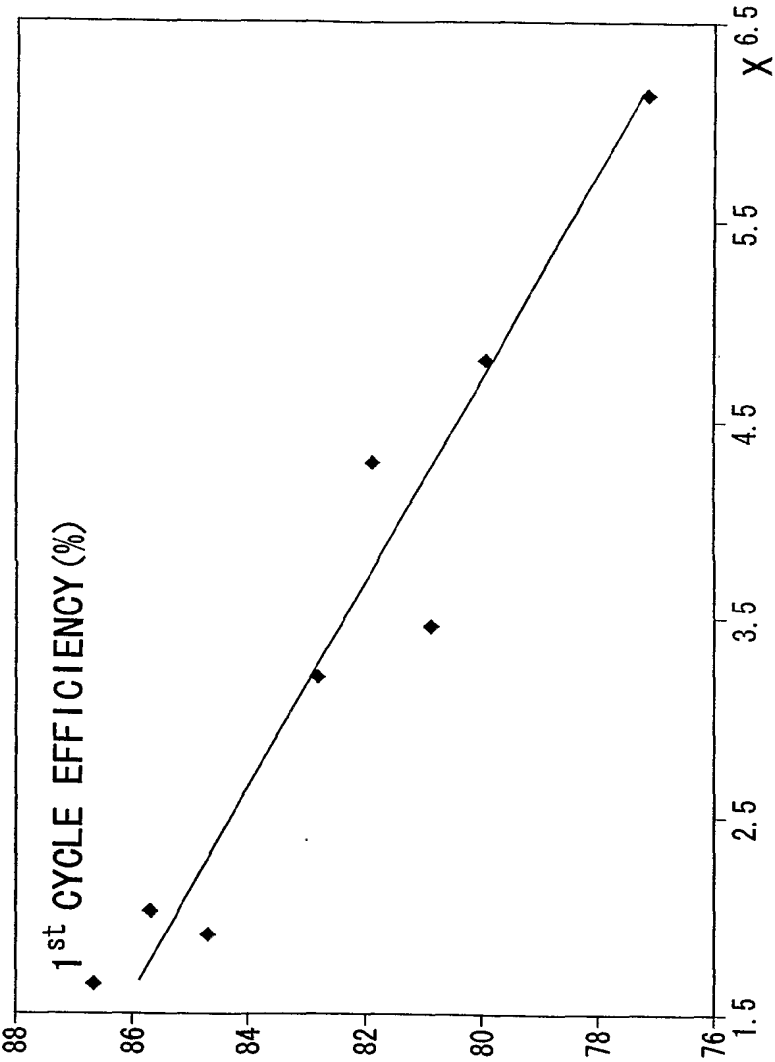


FIG. 21

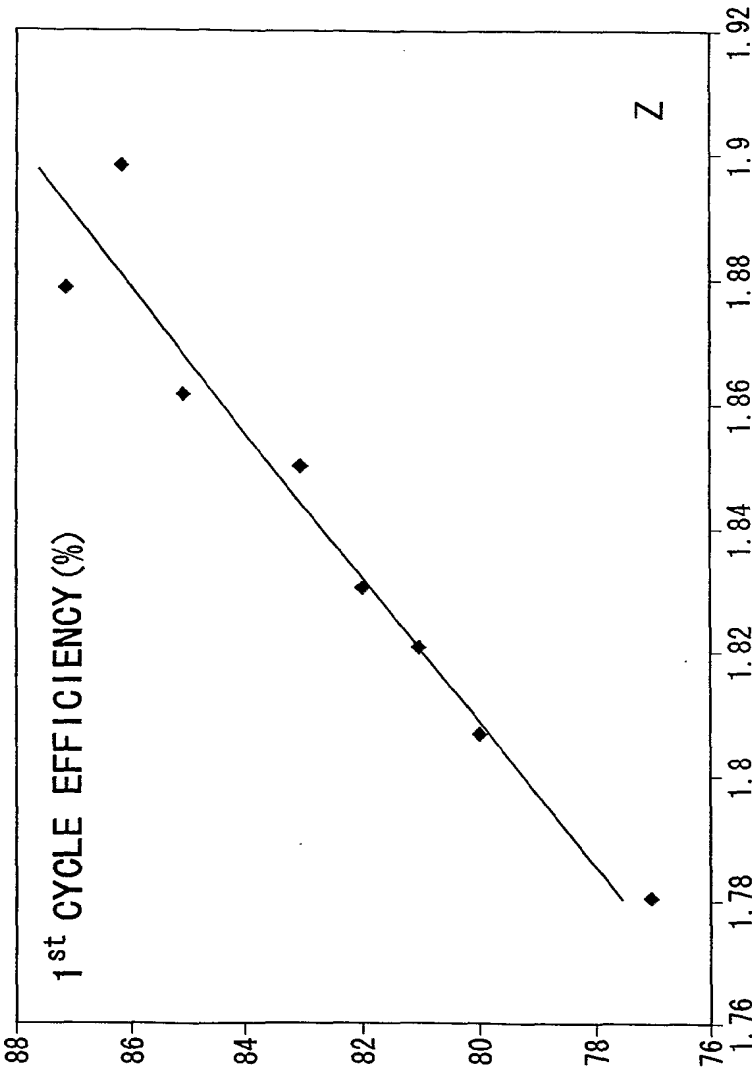


FIG. 22

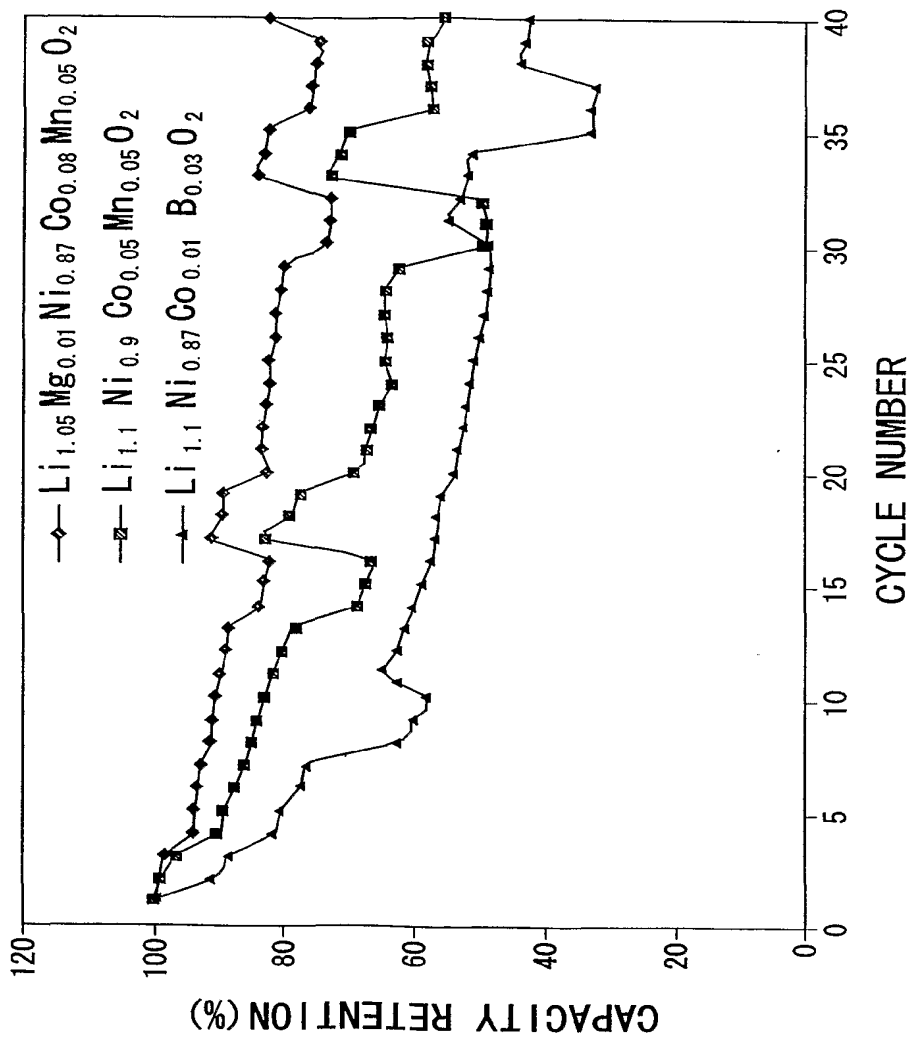


FIG. 23

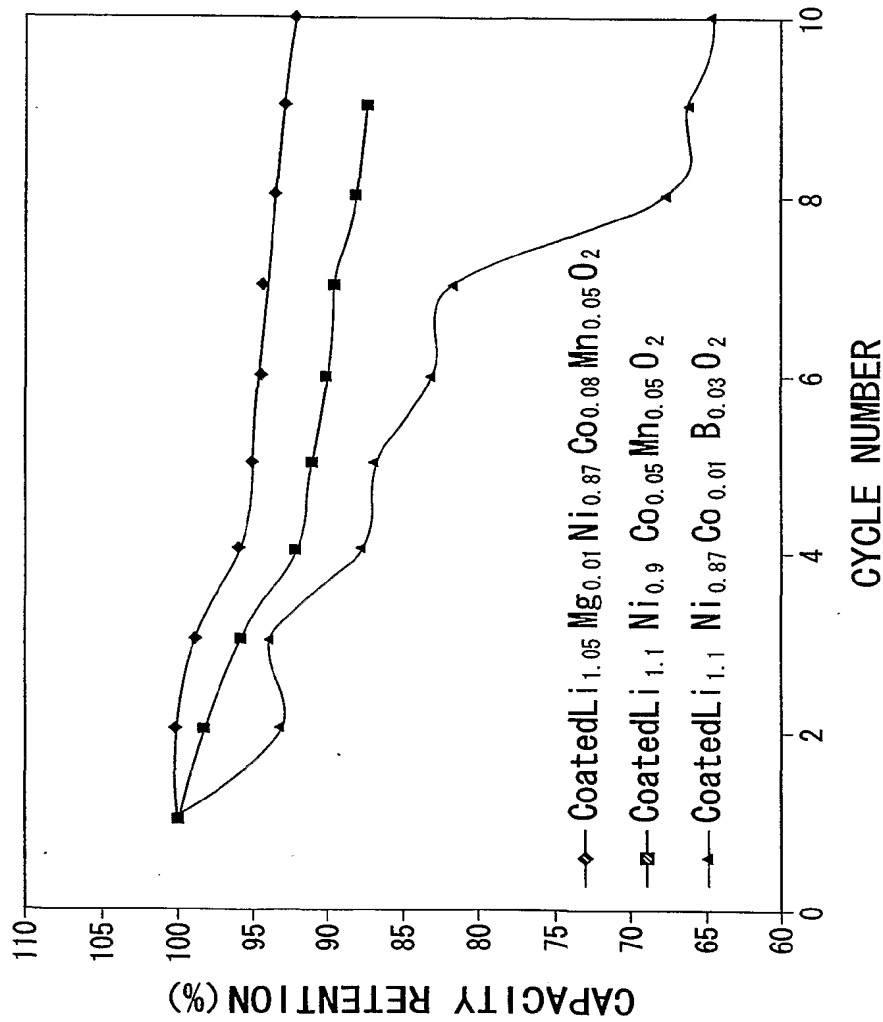


FIG. 24

Electronic Patent Application Fee Transmittal

Application Number:	14865805			
Filing Date:	25-Sep-2015			
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-10103/57			
Filed as Small Entity				
Filing Fees for Utility under 35 USC 111(a)				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Miscellaneous:				
Submission- Information Disclosure Stmt	2806	1	90	90
Total in USD (\$)				90

Electronic Acknowledgement Receipt

EFS ID:	25587940
Application Number:	14865805
International Application Number:	
Confirmation Number:	1076
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-10103/57
Receipt Date:	25-APR-2016
Filing Date:	25-SEP-2015
Time Stamp:	15:47:29
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	\$90
RAM confirmation Number	2294
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		TIA-10103supplDS.PDF	108973	yes	5
			24c3add27c02ba41ec93ea64bd9aca7f9f06a60f		
	Multipart Description/PDF files in .zip description				
	Document Description		Start	End	
	Transmittal Letter		1	3	
	Information Disclosure Statement (IDS) Form (SB08)		4	5	
Warnings:					
Information:					
2	Foreign Reference	WO2005114768A1.pdf	2002071	no	44
			5885a7c0aa951fa5829056a808ef0c52b899bc54		
Warnings:					
Information:					
3	Foreign Reference	WO02103824A2.pdf	2222394	no	70
			0787d8a7e5a5d3a5579edfe46d614f26ddeee971		
Warnings:					
Information:					
4	Fee Worksheet (SB06)	fee-info.pdf	30805	no	2
			71579938025876ac72b340c44cb6fe9be8ec0a78		
Warnings:					
Information:					
Total Files Size (in bytes):			4364243		

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.: 14/865,805

Confirmation No.: 1076

Filed: September 25, 2015

Art Unit: 1767

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

Examiner: P. F. Godenschwager

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT (IDS)

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

Dear Sir:

In accordance with 37 C.F.R. § 1.97, Applicant(s) hereby make of record the following additional documents. A PTO Form SB/08 and a full copy of each of the documents required under 37 C.F.R. § 1.98(a)(2) accompany this statement.

Applicant(s) have become aware of the following documents, cited in an International Search Report issued January 26, 2016, during the prosecution of International Application No. JP2014526041, which corresponds to the above referenced application, and in accordance with 37 C.F.R. § 1.97(c) and (e)(1) or (b)(3), hereby submit(s) these documents for the Examiner's consideration. These documents are cited on the enclosed PTO Form SB/08.

This statement is not to be interpreted as a representation that the cited documents are material, that an exhaustive search has been conducted, or that no other relevant information exists. Nor shall the citation of any document herein be construed *per se* as a representation that

such document is prior art. Moreover, Applicant(s) understand(s) the Examiner will make an independent evaluation of the cited documents.

This Information Disclosure Statement is filed after the mailing date of a Final Office Action or Notice of Allowance, whichever occurred first, but on or before payment of the Issue Fee (37 C.F.R. § 1.97(d)). Applicant(s) hereby petition(s) that the Information Disclosure Statement be considered.

I hereby certify, pursuant to 37 C.F.R. § 1.97(e)(1), that each item of information contained in this Information Disclosure Statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of this Information Disclosure Statement.

Furthermore, in accordance with 37 C.F.R. § 1.704(d), Applicant(s) note(s) that to our knowledge each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart application and that this communication was not received by any individual designated in 37 C.F.R. § 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

Please charge our Credit Card in the amount of \$90.00 covering the fee set forth in 37 C.F.R. § 1.17(p). 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. 04-1133, under Order No. TIA-10103/57.

Dated: April 25, 2016

Respectfully submitted,

Electronic signature: /Weston R. Gould, Ph. D./
Weston R. Gould, Ph. D.
Registration No.: 59,142
DINSMORE & SHOHL LLP
2701 Troy Center Drive, Suite 330
Post Office Box 7021
Troy, Michigan 48007-7021
(248) 647-6000
(248) 647-5210 (Fax)
Attorney for Applicant



UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/865,805	09/25/2015	David Ofer	TIA-10103/57	1076

25006	7590	04/19/2016
DINSMORE & SHOHL LLP		
PO BOX 7021		
TROY, MI 48007-7021		

EXAMINER	
GODENSCHWAGER, PETER F	

ART UNIT	PAPER NUMBER
1767	

NOTIFICATION DATE	DELIVERY MODE
04/19/2016	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

docket@patlaw.com

Response to Rule 312 Communication	Application No. 14/865,805	Applicant(s)
	Examiner	Art Unit

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

1. ☒ The amendment filed on 13 April 2016 under 37 CFR 1.312 has been considered, and has been:

a) ☒ entered.

b) ☐ entered as directed to matters of form not affecting the scope of the invention.

c) ☐ disapproved because the amendment was filed after the payment of the issue fee.

Any amendment filed after the date the issue fee is paid must be accompanied by a petition under 37 CFR 1.313(c)(1) and the required fee to withdraw the application from issue.

d) ☐ disapproved. See explanation below.

e) ☐ entered in part. See explanation below.

K.PAYNE

PUBLISHING DIVISION

Docket No.: TIA-10103/57
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Utility Application of:
David Ofer et al.

Application No.: 14/865,805

Confirmation No.: 1076

Filed: September 25, 2015

Art Unit: 1767

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

Examiner: P.F. Godenschwager

**AMENDMENT IN RESPONSE TO NOTICE TO FILE CORRECTED APPLICATION
PAPERS – NOTICE OF ALLOWANCE MAILED**

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

Dear Sir:

In response to the Notice to File Corrected Application Papers – Notice of Allowance
Mailed, mailed March 16, 2016, Applicant respectfully submits the following instructions to
amend the specification as provided.

AMENDMENTS TO THE SPECIFICATION

Please amend paragraph [0091] to add the period at the end of the last sentence as follows:

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.

REMARKS

By this response, the specification is amended to add missing period at the end of paragraph [0091] that was inadvertently omitted. No new matter has been added.

Applicant believes that no fees are due at this time; however, 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. 04-1133, under Order No. TIA-10103/57.

Dated: April 13, 2016

Respectfully submitted,

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

Registration No.: 59,142
DINSMORE & SHOHL LLP
2701 Troy Center Drive, Suite 330
Post Office Box 7021
Troy, Michigan 48007-7021
(248) 647-6000
(248) 647-5210 (Fax)
Attorney for Applicant

WKA



UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/865,805	09/25/2015	David Ofer	TIA-10103/57	1076

25006 7590 03/16/2016
DINSMORE & SHOHL LLP
PO BOX 7021
TROY, MI 48007-7021

EXAMINER
GODENSCHWAGER, PETER F

ART UNIT PAPER NUMBER
1767

NOTIFICATION DATE DELIVERY MODE
03/16/2016 ELECTRONIC

WKA Correct Spec g: 04-16-16
d: 05-16-16

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

docket@patlaw.com

RECEIVED
MAR 16 2016



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

Application No. : 14865805
Applicant : Ofer
Filing Date : 09/25/2015
Date Mailed : 03/16/2016

NOTICE TO FILE CORRECTED APPLICATION PAPERS

Notice of Allowance Mailed

This application has been accorded an Allowance Date and is being prepared for issuance. The application, however, is incomplete for the reasons below.

Applicant is given two (2) months from the mail date of this Notice within which to respond. This time period for reply is extendable under 37 CFR 1.136(a) for only TWO additional MONTHS.

The informalities requiring correction are indicated in the attachment(s). If the informality pertains to the abstract, specification (including claims) or drawings, the informality must be corrected with an amendment in compliance with 37 CFR 1.121 (or, if the application is a reissue application, 37 CFR 1.173). Such an amendment may be filed after payment of the issue fee if limited to correction of informalities noted herein. See Waiver of 37 CFR 1.312 for Documents Required by the Office of Patent Publication, 1280 Off. Gaz. Patent Office 918 (March 23, 2004). In addition, if the informality is not corrected until after payment of the issue fee, for purposes of 35 U.S.C. 154(b)(1)(iv), "all outstanding requirements" will be considered to have been satisfied when the informality has been corrected. A failure to respond within the above-identified time period will result in the application being ABANDONED.

See attachment(s).

*A copy of this notice **MUST** be returned with the reply. Please address response to
"Mail Stop Issue Fee, Commissioner for Patents,
P.O. Box 1450, Alexandria, VA 22313-1450".*

/Stephanie Smart/
Publication Branch
Office of Data Management
(571) 272-4200

Application No. 14865805

**IDENTIFICATION OF APPLICATION DEFICIENCIES
IN APPLICATION FILED ON OR AFTER SEPTEMBER 16, 2012**

- ☐ Applicant must provide legible text for the following item(s).
- ☐ Specification filed , page(s) .
- ☐ Claims filed , claim(s) .
- ☐ Other: .
- ☒ Applicant must provide missing information on the following page(s) of the specification by amending the specification to add the missing text. No new matter may be added.
Page/line no(s). page 25 line 2
- ☐ The specification refers to one or more applications by attorney docket number and does not show the U.S. application number(s). Applicant must supply the U.S. application number in place of each attorney docket number.
Page/line no(s).
- ☐ Applicant must provide an Abstract of the Disclosure.
- ☐ The Application Data Sheet (ADS dated) does not supply the inventor's city and/or does not supply the inventor's U.S. state and/or does not supply the inventor's country. Applicant must submit a signed application data sheet that corrects this deficiency. To be in compliance with 37 CFR 1.76, the corrected application data sheet must identify the information being changed by using underlining for additions and strikethroughs or brackets for deletions..
- ☐ The Application Data Sheet (ADS dated) was not properly signed. Applicant must submit an application data sheet that is properly signed in accordance with 37 CFR 1.76(e) and 1.33(b). If the unsigned application data sheet shows foreign priority information or domestic benefit information, and if the Office does not show foreign priority information or domestic benefit information on the filing receipt, applicant may need to file a petition under 37 CFR 1.55 or 1.78 for delayed claim for priority or benefit if the claim for priority or benefit has not been filed in accordance with the time periods set forth in 37 CFR 1.55 or 1.78.
- ☐ Other:

Electronic Acknowledgement Receipt

EFS ID:	25479817
Application Number:	14865805
International Application Number:	
Confirmation Number:	1076
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-10103/57
Receipt Date:	13-APR-2016
Filing Date:	25-SEP-2015
Time Stamp:	14:50:42
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no
------------------------	----

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Supplemental Response or Supplemental Amendment	TIA10103response.PDF	111222 54a3a7218d1744348cbb7d3fa3646d514e87e6e	no	6

Warnings:

Information:

POSCO Future M v. TIAX LLC

POSCO Future M EX1004

Page 149

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

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

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/865,805	09/25/2015	David Ofer	TIA-10103/57	1076
25006 7590 03/16/2016 DINSMORE & SHOHL LLP PO BOX 7021 TROY, MI 48007-7021			EXAMINER GODENSCHWAGER, PETER F	
			ART UNIT 1767	PAPER NUMBER
			NOTIFICATION DATE 03/16/2016	DELIVERY MODE ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

docket@patlaw.com



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

Application No. : 14865805
Applicant : Ofer
Filing Date : 09/25/2015
Date Mailed : 03/16/2016

NOTICE TO FILE CORRECTED APPLICATION PAPERS

Notice of Allowance Mailed

This application has been accorded an Allowance Date and is being prepared for issuance. The application, however, is incomplete for the reasons below.

Applicant is given two (2) months from the mail date of this Notice within which to respond. This time period for reply is extendable under 37 CFR 1.136(a) for only TWO additional MONTHS.

The informalities requiring correction are indicated in the attachment(s). If the informality pertains to the abstract, specification (including claims) or drawings, the informality must be corrected with an amendment in compliance with 37 CFR 1.121 (or, if the application is a reissue application, 37 CFR 1.173). Such an amendment may be filed after payment of the issue fee if limited to correction of informalities noted herein. See Waiver of 37 CFR 1.312 for Documents Required by the Office of Patent Publication, 1280 Off. Gaz. Patent Office 918 (March 23, 2004). In addition, if the informality is not corrected until after payment of the issue fee, for purposes of 35 U.S.C. 154(b)(1)(iv), "all outstanding requirements" will be considered to have been satisfied when the informality has been corrected. A failure to respond within the above-identified time period will result in the application being ABANDONED.

See attachment(s).

*A copy of this notice **MUST** be returned with the reply. Please address response to
"Mail Stop Issue Fee, Commissioner for Patents,
P.O. Box 1450, Alexandria, VA 22313-1450".*

/Stephanie Smart/
Publication Branch
Office of Data Management
(571) 272-4200

**IDENTIFICATION OF APPLICATION DEFICIENCIES
IN APPLICATION FILED ON OR AFTER SEPTEMBER 16, 2012**

- ☐ Applicant must provide legible text for the following item(s).
- ☐ Specification filed , page(s) .
- ☐ Claims filed , claim(s) .
- ☐ Other: .
- ☒ Applicant must provide missing information on the following page(s) of the specification by amending the specification to add the missing text. No new matter may be added.
Page/line no(s). page 25 line 2
- ☐ The specification refers to one or more applications by attorney docket number and does not show the U.S. application number(s). Applicant must supply the U.S. application number in place of each attorney docket number.
Page/line no(s).
- ☐ Applicant must provide an Abstract of the Disclosure.
- ☐ The Application Data Sheet (ADS dated) does not supply the inventor's city and/or does not supply the inventor's U.S. state and/or does not supply the inventor's country. Applicant must submit a signed application data sheet that corrects this deficiency. To be in compliance with 37 CFR 1.76, the corrected application data sheet must identify the information being changed by using underlining for additions and strikethroughs or brackets for deletions..
- ☐ The Application Data Sheet (ADS dated) was not properly signed. Applicant must submit an application data sheet that is properly signed in accordance with 37 CFR 1.76(e) and 1.33(b). If the unsigned application data sheet shows foreign priority information or domestic benefit information, and if the Office does not show foreign priority information or domestic benefit information on the filing receipt, applicant may need to file a petition under 37 CFR 1.55 or 1.78 for delayed claim for priority or benefit if the claim for priority or benefit has not been filed in accordance with the time periods set forth in 37 CFR 1.55 or 1.78.
- ☐ Other:



UNITED STATES PATENT AND TRADEMARK OFFICE

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

NOTICE OF ALLOWANCE AND FEE(S) DUE

25006 7590 03/10/2016
DINSMORE & SHOHL LLP
PO BOX 7021
TROY, MI 48007-7021

EXAMINER

GODENSCHWAGER, PETER F

ART UNIT

PAPER NUMBER

1767

DATE MAILED: 03/10/2016

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
-----------------	-------------	----------------------	---------------------	------------------

14/865,805

09/25/2015

David Ofer

TIA-10103/57

1076

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

06/10/2016

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 03/10/2016
DINSMORE & SHOHL LLP
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.
14/865,805	09/25/2015	David Ofer	TIA-10103/57	1076

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	06/10/2016

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
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/865,805	09/25/2015	David Ofer	TIA-10103/57	1076
25006 7590 03/10/2016 DINSMORE & SHOHL LLP PO BOX 7021 TROY, MI 48007-7021			EXAMINER GODENSCHWAGER, PETER F	
			ART UNIT	PAPER NUMBER
			1767	
DATE MAILED: 03/10/2016				

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. 14/865,805	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 reply filed February 26, 2016.
☐ 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 1-17. 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>2/26/2016</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

Terminal Disclaimer

The terminal disclaimer filed on February 26, 2016 disclaiming the terminal portion of any patent granted on this application which would extend beyond the expiration date of US Patent No. 9,209,455 has been reviewed and is accepted. The terminal disclaimer has been recorded.

Allowable Subject Matter

Claims 1-17 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 - NaFeO_2 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

Art Unit: 1767

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.

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
March 3, 2016

Doc code: IDS

Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)

Approved for use through 07/31/2016. OMB 0651-0031

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

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

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)	Application Number		14865805	
	Filing Date		2015-09-25	
	First Named Inventor	David Ofer		
	Art Unit	1767		
	Examiner Name	Peter F. Godenschwager		
	Attorney Docket Number	TIA-10103/57		

U.S.PATENTS						
Examiner Initial*	Cite No	Patent Number	Kind Code ¹	Issue Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1	9209455	A1	2015-12-08	Ofer et al.	

If you wish to add additional U.S. Patent citation information please click the Add button.

U.S.PATENT APPLICATION PUBLICATIONS						
Examiner Initial*	Cite No	Publication Number	Kind Code ¹	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1	20050181280		2005-08-18	Ceder et al.	
	2	20090104530		2009-04-23	Shizuka et al.	

If you wish to add additional U.S. Published Application citation information please click the Add button.

FOREIGN PATENT DOCUMENTS								
Examiner Initial*	Cite No	Foreign Document Number ³	Country Code ²	Kind Code ⁴	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear	T ⁵
	1	2008234872	JP	A	2008-10-02	Sony Corp		☒
	2	1020100099668	KR		2010-09-13	Sony Corp.		☒

**INFORMATION DISCLOSURE
STATEMENT BY APPLICANT**
(Not for submission under 37 CFR 1.99)

Application Number	14865805
Filing Date	2015-09-25
First Named Inventor	David Ofer
Art Unit	1767
Examiner Name	Peter F. Godenschwager
Attorney Docket Number	TIA-10103/57

If you wish to add additional Foreign Patent Document citation information please click the Add button

NON-PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T ⁵
	1		☐

If you wish to add additional non-patent literature document citation information please click the Add button

EXAMINER SIGNATURE

Examiner Signature	/PETER F GODENSCHWAGER/	Date Considered	03/03/2016
--------------------	-------------------------	-----------------	------------

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

¹ See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. ² Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). ³ For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. ⁴ Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. ⁵ Applicant is to place a check mark here if English language translation is attached.

Search Notes 	Application/Control No. 14865805	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	12/21/2015	PFG
H01M 4/364; 3/366	3/2/2016	PFG

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

SEARCH NOTES		
Search Notes	Date	Examiner
inventor name search (PALM)	12/21/2015	PFG
EAST search (see attached)	12/21/2015	PFG
EAST search (see attached)	3/3/2016	PFG

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner
H01M 4/364; 3/366		3/3/2016	PFG

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

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S30	9063	H01M4/364.CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2016/03/02 10:26
S31	14615	H01M4/366.CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2016/03/02 10:26

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L2	2133	H01M4/364.CPC.	US-PGPUB; USPAT	ADJ	ON	2016/03/03 08:50
L3	3692	H01M4/366.CPC.	US-PGPUB; USPAT	ADJ	ON	2016/03/03 08:50
L4	2	(crystallite AND particle AND (lithium OR Li) AND (nickel OR Ni) AND grain boundary AND ("alpha-NaFeO.sub.2" OR "NaFeO.sub.2"))).clm.	US-PGPUB	ADJ	ON	2016/03/03 08:58
L5	2	(crystallite AND particle AND grain boundary AND ("alpha-NaFeO.sub.2" OR "NaFeO.sub.2"))).clm.	US-PGPUB	ADJ	ON	2016/03/03 08:59

3/ 3/ 2016 9:24:51 AM
C:\ Users\ pgodenschwager\ Documents\ EAST\ Workspaces\ 14_238643.wsp

Issue Classification 	Application/Control No. 14865805	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	I	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
C01G		53	/	66	I	2013-01-01
H01M		2004	/	028	A	2013-01-01

CPC Combination Sets				
Symbol	Type	Set	Ranking	Version

NONE		Total Claims Allowed:	
(Assistant Examiner)		17	
(Date)			
/PETER F GODENSCHWAGER/ Primary Examiner.Art Unit 1767	03/03/2016	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification 	Application/Control No. 14865805	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	10	17												
2	2														
3	3														
4	4														
5	5														
6	6														
7	7														
8	8														
9	9														
11	10														
12	11														
13	12														
14	13														
15	14														
16	15														
17	16														

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	17	
/PETER F GODENSCHWAGER/ Primary Examiner.Art Unit 1767	03/03/2016	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 14/865,805	Filing Date 09/25/2015	☐ To be Mailed
---	---	----------------------------------	---------------------------------------

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	02/26/2016	CLAIMS REMAINING AFTER AMENDMENT	MINUS	HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE (\$)	ADDITIONAL FEE (\$)
	Total (37 CFR 1.16(i))	* 20	Minus	** 20	= 0	x \$40 =	0
	Independent (37 CFR 1.16(h))	* 1	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.

LIE
/ALLYSON PURNELL/

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.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Docket No.: TIA-10103/57
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Utility Application of:
David Ofer et al.

Application No.: 14/865,805

Confirmation No.: 1076

Filed: September 25, 2015

Art Unit: 1767

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

Examiner: GODENSCHWAGER,
PETER F

**AMENDMENT IN RESPONSE TO NON-FINAL
OFFICE ACTION UNDER 37 C.F.R. 1.111**

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

Dear Sir:

INTRODUCTORY COMMENTS

In response to the Office Action dated December 24, 2015, please amend the above-identified U.S. patent application as follows:

AMENDMENTS TO THE CLAIMS

1. (Original) A particle, comprising:
a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising:
lithium, nickel, and oxygen;
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. (Original) 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. (Original) 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. (Original) 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. (Original) 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 1 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. (Original) 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. (Original) The particle of claims 1 or 7, wherein the first composition further contains cobalt, with the cobalt concentration in the range of 0 to about 0.5 mole per mole of the first composition.

9. (Currently Amended) The particle of claim 8 wherein the first composition further contains cobalt, with the cobalt concentration in the range of 0.0 to about 0.3 mole per mole of the first composition.

10. (Original) 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.

11. (Currently Amended) The particle of claims 1 or 7, ~~or 9~~, wherein said first composition comprises nickel at a concentration of 0.8 to 1 moles per mole of said first composition.

12. (Original) The particle of claim 11 wherein said first composition comprises nickel at a concentration of 0.92 moles per mole of said first composition.

13. (Original) The particle of claims 1 or 7 wherein the first composition comprises:

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 0.99 mole, per mole of the first composition;
and
cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition.

14. (Original) The particle of claims 1 or 7 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.

15. (Original) 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, Li, Al, Ti, B, or Si, or a combination thereof.

16. (Original) A method of manufacturing the particle of claim 1, 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; 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.

17. (New) The particle of claim 9, wherein said first composition comprises nickel at a concentration of 0.8 to 1 moles per mole of said first composition.

REMARKS

Applicants appreciate the detail and thoroughness of the examination embodied in the Office Action of Paper No. 20151221 ("Office Action"). This paper is believed to be fully responsive to the Office Action.

With entry of this paper, claim 17 is newly presented and claims 1-16 remain pending and under examination.

Claim 9 is currently amended to correct a typographical error to include a period.

Claim 11 is currently amended to refer to claims 1 and 7.

Claim 17 is newly presented reciting the elements of claim 11 as originally presented and to depend from claim 9 also as originally presented in claim 11.

It is believed that no new matter is added by way of amendment.

Remarks to the objections to claims 11 and 12

Claim 11 is currently amended to refer to claims 1 and 7. It is believed that this amendment fully addresses the claim objections. Reconsideration and withdrawal of the objections to claims 11 and 12 are respectfully requested.

Remarks to the Rejection of Non-Statutory Double Patenting

Claims 10 and 13-16 are rejected under on the grounds of non-statutory double patenting over claims 1-14 of U.S. Patent No. 9,209,455.

In view of the terminal disclaimer filed concurrently with this paper, reconsideration and withdrawal of the rejections of claims 1-10 and 13-16 are respectfully requested.

Summary

Applicant submits that all claims are in allowable form and directed to patentable subject matter. Reconsideration of the outstanding rejections and passing of all claims to allowance are solicited. Additional bases of patentability exist, and Applicant reserves the right to make these of record in the course of prosecution as necessary.

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. 04-1133.

Dated: February 24, 2016

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

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Utility Application of:
David Ofer et al.

Application No.: 14/865,805

Confirmation No.: 1076

Filed: September 25, 2015

Art Unit: 1767

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

Examiner: Godenschwager, Peter F.

INFORMATION DISCLOSURE STATEMENT (IDS)

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

Dear Sir:

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 is filed more than three months after the U.S. filing date, OR more than three months after the date of entry of the national stage of a PCT application, AND after the mailing date of the first Office Action on the merits, whichever occurs first, but before the mailing date of any of a Final Office Action, a Notice of Allowance (37 C.F.R. § 1.97(c)) or an action that otherwise closes prosecution in the application.

Copies of the references on the PTO/SB/08 are not provided.

The following documents cited in the attached form PTO/SB/08:

Doc Number	Ctry	Non-Patent Literature Documents
2008234872	JP	
1020100099668	KR	

are not supplied because they were previously cited by or submitted to the Office in prior application number 14/238,643 filed February 12, 2014 and relied upon in this application for an earlier filing date under 35 U.S.C. § 120.

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.

Please charge our Credit Card in the amount of \$90.00 covering the fee set forth in 37 C.F.R. § 1.17(p). 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. 04-1133, under Order No. TIA-10103/57.

Dated: February 25, 2016

Respectfully submitted,

Electronic signature: /Weston R. Gould/
Weston R. Gould
Registration No.: 59,142
DINSMORE & SHOHL LLP
2701 Troy Center Drive, Suite 330
Post Office Box 7021
Troy, Michigan 48007-7021
(734) 913-9300
(734) 913-6007 (Fax)
Attorney for Applicant

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)	Application Number		14865805	
	Filing Date		2015-09-25	
	First Named Inventor	David Ofer		
	Art Unit	1767		
	Examiner Name	Peter F. Godenschwager		
	Attorney Docket Number	TIA-10103/57		

U.S.PATENTS						
Examiner Initial*	Cite No	Patent Number	Kind Code ¹	Issue Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1	9209455	A1	2015-12-08	Ofer et al.	

If you wish to add additional U.S. Patent citation information please click the Add button.

U.S.PATENT APPLICATION PUBLICATIONS						
Examiner Initial*	Cite No	Publication Number	Kind Code ¹	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1	20050181280		2005-08-18	Ceder et al.	
	2	20090104530		2009-04-23	Shizuka et al.	

If you wish to add additional U.S. Published Application citation information please click the Add button.

FOREIGN PATENT DOCUMENTS								
Examiner Initial*	Cite No	Foreign Document Number ³	Country Code ²	Kind Code ⁴	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear	T ⁵
	1	2008234872	JP	A	2008-10-02	Sony Corp		☒
	2	1020100099668	KR		2010-09-13	Sony Corp.		☒

**INFORMATION DISCLOSURE
STATEMENT BY APPLICANT**
(Not for submission under 37 CFR 1.99)

Application Number	14865805
Filing Date	2015-09-25
First Named Inventor	David Ofer
Art Unit	1767
Examiner Name	Peter F. Godenschwager
Attorney Docket Number	TIA-10103/57

If you wish to add additional Foreign Patent Document citation information please click the Add button

NON-PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T ⁵
	1		☐

If you wish to add additional non-patent literature document citation information please click the Add button

EXAMINER SIGNATURE

Examiner Signature		Date Considered	
--------------------	--	-----------------	--

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

¹ See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. ² Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). ³ For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. ⁴ Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. ⁵ Applicant is to place a check mark here if English language translation is attached.

**INFORMATION DISCLOSURE
STATEMENT BY APPLICANT**
(Not for submission under 37 CFR 1.99)

Application Number	14865805
Filing Date	2015-09-25
First Named Inventor	David Ofer
Art Unit	1767
Examiner Name	Peter F. Godenschwager
Attorney Docket Number	TIA-10103/57

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☒ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Weston R. Gould, Ph. D./	Date (YYYY-MM-DD)	2016-02-25
Name/Print	Weston R. Gould, Ph. D.	Registration Number	59142

This collection of information is required by 37 CFR 1.97 and 1.98. 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 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Electronic Patent Application Fee Transmittal

Application Number:	14865805			
Filing Date:	25-Sep-2015			
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-10103/57			
Filed as Small Entity				
Filing Fees for Utility under 35 USC 111(a)				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Miscellaneous:				
Submission- Information Disclosure Stmt	2806	1	90	90
Total in USD (\$)				90

Electronic Acknowledgement Receipt

EFS ID:	25035081
Application Number:	14865805
International Application Number:	
Confirmation Number:	1076
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-10103/57
Receipt Date:	26-FEB-2016
Filing Date:	25-SEP-2015
Time Stamp:	14:55:56
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	\$90
RAM confirmation Number	1274
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		doc00806020160226145342.pdf	700802	yes	14
			c697ad09cf766b86d8fea4d3712360bf8748e826		
	Multipart Description/PDF files in .zip description				
	Document Description		Start	End	
	Miscellaneous Incoming Letter		1	1	
	Amendment/Req. Reconsideration-After Non-Final Reject		2	8	
	Transmittal Letter		9	11	
	Information Disclosure Statement (IDS) Form (SB08)		12	14	
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	30804	no	2
			ba4908398305b1b37749822ff9e96f73532fdaca		
Warnings:					
Information:					
Total Files Size (in bytes):			731606		

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.

AMENDMENT TRANSMITTAL LETTER			Docket No. TIA-10103/57	
Application No. 14/865,805-Conf. #1076	Filing Date September 25, 2015	Examiner Not Yet Assigned	Art Unit N/A	

Applicant(s): David Ofer et al.

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

TO THE COMMISSIONER FOR PATENTS

Transmitted herewith is an amendment in the above-identified application.
The fee has been calculated and is transmitted as shown below.

CLAIMS AS AMENDED					
	Claims Remaining After Amendment	Highest Number Previously Paid	Number Extra Claims Present	Rate	
Total Claims	17	- 20 =	0	x	
Independent Claims	2	- 3 =	0	x	
Multiple Dependent Claims (check if applicable) ☐					
Other fee (please specify):					
TOTAL ADDITIONAL FEE FOR THIS AMENDMENT:					0.00

☐ Large Entity
 ☒ Small Entity

☒ No additional fee is required for this amendment.

☐ Please charge Deposit Account No. _____ in the amount of \$ _____.

☐ A check in the amount of \$ _____ to cover the filing fee is enclosed.

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

☒ The Director is hereby authorized to charge and credit Deposit Account No. 04-1133 as described below. A duplicate copy of this sheet is enclosed.

☒ Credit any overpayment.

☒ Charge any additional filing or application processing fees required under 37 C.F.R. § 1.16 and 1.17.

/Weston R. Gould, Ph. D./

Weston R. Gould, Ph. D.

Attorney/Agent Reg. No.: 59,142

DINSMORE & SHOHL LLP

2701 Troy Center Drive, Suite 330

Post Office Box 7021

Troy, Michigan 48007-7021

(248) 647-6000

Dated: February 26, 2016

Doc Code: DIST.E.FILE Document Description: Electronic Terminal Disclaimer - Filed		PTO/SB/26 U.S. Patent and Trademark Office Department of Commerce
Electronic Petition Request	TERMINAL DISCLAIMER TO OBIATE A DOUBLE PATENTING REJECTION OVER A "PRIOR" PATENT	
Application Number	14865805	
Filing Date	25-Sep-2015	
First Named Inventor	David Ofer	
Attorney Docket Number	TIA-10103/57	
Title of Invention	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME	
☒ Filing of terminal disclaimer does not obviate requirement for response under 37 CFR 1.111 to outstanding Office Action ☒ This electronic Terminal Disclaimer is not being used for a Joint Research Agreement.		
Owner	Percent Interest	
TIAX, LLC	100%	
The owner(s) with percent interest listed above in the instant application hereby disclaims, except as provided below, the terminal part of the statutory term of any patent granted on the instant application which would extend beyond the expiration date of the full statutory term of prior patent number(s) 9209455 as the term of said prior patent is presently shortened by any terminal disclaimer. The owner hereby agrees that any patent so granted on the instant application shall be enforceable only for and during such period that it and the prior patent are commonly owned. This agreement runs with any patent granted on the instant application and is binding upon the grantee, its successors or assigns. In making the above disclaimer, the owner does not disclaim the terminal part of the term of any patent granted on the instant application that would extend to the expiration date of the full statutory term of the prior patent, "as the term of said prior patent is presently shortened by any terminal disclaimer," in the event that said prior patent later: - expires for failure to pay a maintenance fee; - is held unenforceable; - is found invalid by a court of competent jurisdiction; - is statutorily disclaimed in whole or terminally disclaimed under 37 CFR 1.321; - has all claims canceled by a reexamination certificate; - is reissued; or - is in any manner terminated prior to the expiration of its full statutory term as presently shortened by any terminal disclaimer. ☒ Terminal disclaimer fee under 37 CFR 1.20(d) is included with Electronic Terminal Disclaimer request.		

☐ I certify, in accordance with 37 CFR 1.4(d)(4), that the terminal disclaimer fee under 37 CFR 1.20(d) required for this terminal disclaimer has already been paid in the above-identified application.	
Applicant claims the following fee status:	
☒ Small Entity ☐ Micro Entity ☐ Regular Undiscounted	
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.	
THIS PORTION MUST BE COMPLETED BY THE SIGNATORY OR SIGNATORIES I certify, in accordance with 37 CFR 1.4(d)(4) that I am:	
☒ An attorney or agent registered to practice before the Patent and Trademark Office who is of record in this application Registration Number <u>59142</u>	
☐ A sole inventor	
☐ A joint inventor; I certify that I am authorized to sign this submission on behalf of all of the inventors as evidenced by the power of attorney in the application	
☐ A joint inventor; all of whom are signing this request	
Signature	/Weston R. Gould/
Name	Weston R. Gould

*Statement under 37 CFR 3.73(b) is required if terminal disclaimer is signed by the assignee (owner).
 Form PTO/SB/96 may be used for making this certification. See MPEP § 324.

Electronic Patent Application Fee Transmittal

Application Number:	14865805			
Filing Date:	25-Sep-2015			
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-10103/57			
Filed as Small Entity				
Filing Fees for Utility under 35 USC 111(a)				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Statutory or Terminal Disclaimer	2814	1	160	160
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Extension-of-Time:				
Miscellaneous:				
Total in USD (\$)				160

Doc Code: DISQ.E.FILE

Document Description: Electronic Terminal Disclaimer – Approved

Application No.: 14865805

Filing Date: 25-Sep-2015

Applicant/Patent under Reexamination: Ofer et al.

Electronic Terminal Disclaimer filed on February 26, 2016

☒ APPROVED

This patent is subject to a terminal disclaimer

☐ DISAPPROVED

Approved/Disapproved by: Electronic Terminal Disclaimer automatically approved by EFS-Web

U.S. Patent and Trademark Office

Electronic Acknowledgement Receipt

EFS ID:	25035191
Application Number:	14865805
International Application Number:	
Confirmation Number:	1076
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-10103/57
Receipt Date:	26-FEB-2016
Filing Date:	25-SEP-2015
Time Stamp:	15:02:14
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	\$ 160
RAM confirmation Number	1381
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	Electronic Terminal Disclaimer-Filed	eTerminal-Disclaimer.pdf	33574	no	2
			da84aeb6db9d8e9afe94340fc1052b459c60d749		
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30582	no	2
			5a0e9a9b31f891967f4af9fb243af9dcfe185ea7		
Warnings:					
Information:					
Total Files Size (in bytes):			64156		
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.					



UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
14/865,805	09/25/2015	David Ofer	TIA-10103/57

CONFIRMATION NO. 1076

PUBLICATION NOTICE



OC000000079921862

25006
DINSMORE & SHOHL LLP
PO BOX 7021
TROY, MI 48007-7021

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

Publication No.US-2016-0013475-A1

Publication Date:01/14/2016

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



UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/865,805	09/25/2015	David Ofer	TIA-10103/57	1076

25006 7590 12/24/2015
DINSMORE & SHOHL LLP
PO BOX 7021
TROY, MI 48007-7021

EXAMINER

GODENSCHWAGER, PETER F

ART UNIT	PAPER NUMBER
----------	--------------

1767

NOTIFICATION DATE	DELIVERY MODE
-------------------	---------------

12/24/2015

ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

docket@patlaw.com

Office Action Summary	Application No. 14/865,805	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 --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 25 September 2015.
☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on ____.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ 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.
- 4) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

- 5) ☒ Claim(s) 1-16 is/are pending in the application.
5a) Of the above claim(s) ____ is/are withdrawn from consideration.
- 6) ☐ Claim(s) ____ is/are allowed.
- 7) ☒ Claim(s) 1-10 and 13-16 is/are rejected.
- 8) ☒ Claim(s) 11 and 12 is/are objected to.
- 9) ☐ Claim(s) ____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, 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.

Application Papers

- 10) ☐ The specification is objected to by the Examiner.
- 11) ☐ The drawing(s) filed on ____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

- 12) ☐ 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)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- | | |
|---|---|
| 1) ☒ Notice of References Cited (PTO-892) | 3) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date. ____. |
| 2) ☐ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b)
Paper No(s)/Mail Date ____. | 4) ☐ Other: ____. |

DETAILED ACTION

Notice of Pre-AIA or AIA Status

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

Claim Objections

Claims 11 and 12 are objected to under 37 CFR 1.75(c) as being in improper form because a multiple dependent claim may not depend from another multiple dependent claim. See MPEP § 608.01(n). Accordingly, the claims 11 and 12 have not been further treated on the merits.

Double Patenting

The nonstatutory double patenting rejection is based on a judicially created doctrine grounded in public policy (a policy reflected in the statute) so as to prevent the unjustified or improper timewise extension of the “right to exclude” granted by a patent and to prevent possible harassment by multiple assignees. A nonstatutory double patenting rejection is appropriate where the claims at issue are not identical, but at least one examined application claim is not patentably distinct from the reference claim(s) because the examined application claim is either anticipated by, or would have been obvious over, the reference claim(s). See, e.g., *In re Berg*, 140 F.3d 1428, 46 USPQ2d 1226 (Fed. Cir. 1998); *In re Goodman*, 11 F.3d 1046, 29 USPQ2d 2010 (Fed. Cir. 1993); *In re Longi*, 759 F.2d 887, 225 USPQ 645 (Fed. Cir. 1985); *In re Van Ornum*, 686 F.2d 937, 214 USPQ 761 (CCPA 1982); *In re Vogel*, 422 F.2d 438, 164 USPQ 619 (CCPA 1970); and *In re Thorington*, 418 F.2d 528, 163 USPQ 644 (CCPA 1969).

A timely filed terminal disclaimer in compliance with 37 CFR 1.321(c) or 1.321(d) may be used to overcome an actual or provisional rejection based on a nonstatutory double patenting ground provided the reference application or patent either is shown to be commonly owned with this application, or claims an invention made as a result of activities undertaken within the scope of a joint research agreement. See MPEP § 717.02 for applications subject to examination under the first inventor to file provisions of the AIA as explained in MPEP § 2159. See MPEP §§ 706.02(l)(1) - 706.02(l)(3) for applications not subject to examination under the first inventor to file provisions of the AIA. A terminal disclaimer must be signed in compliance with 37 CFR 1.321(b).

The USPTO Internet website contains terminal disclaimer forms which may be used. Please visit www.uspto.gov/forms/. The filing date of the application in which the form is filed determines what form (e.g., PTO/SB/25, PTO/SB/26, PTO/AIA/25, or PTO/AIA/26) should be used. A web-based eTerminal Disclaimer may be filled out completely online using web-screens. An eTerminal Disclaimer that meets all requirements is auto-processed and approved immediately upon submission. For more information about eTerminal Disclaimers, refer to <http://www.uspto.gov/patents/process/file/efs/guidance/eTD-info-I.jsp>.

Claims 1-10 and 13-16 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-14 of U.S. Patent No. 9,209,455. Although the claims at issue are not identical, they are not patentably distinct from each other because the patented claims anticipate the pending claims as the patented claims are narrower in scope than the pending claims.

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.

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
December 21, 2015

Notice of References Cited	Application/Control No. 14/865,805		Applicant(s)/Patent Under Reexamination OFER ET AL.	
	Examiner PETER F. GODENSCHWAGER		Art Unit 1767	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
*	A	US-2009/0104530 A1	04-2009	Shizuka; Kenji	H01M4/505	429/223
	B	US-				
	C	US-				
	D	US-				
	E	US-				
	F	US-				
	G	US-				
	H	US-				
	I	US-				
	J	US-				
	K	US-				
	L	US-				
	M	US-				

FOREIGN PATENT DOCUMENTS

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

NON-PATENT DOCUMENTS

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

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



UNITED STATES PATENT AND TRADEMARK OFFICE

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

BIB DATA SHEET

CONFIRMATION NO. 1076

SERIAL NUMBER	FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.		
14/865,805	09/25/2015	252	1767	TIA-10103/57		
APPLICANTS TIAX LLC, Lexington, MA;						
INVENTORS David Ofer, Needham, MA; Adrian W. Pullen, Boston, MA; /PFG/ Suresh Sriramulu, Arlington, MA;						
** CONTINUING DATA ***** This application is a DIV of 14/238,643 02/12/2014 PAT 9209455 which 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 ** 10/08/2015						
Foreign Priority claimed 35 USC 119(a-d) conditions met Verified and Acknowledged	☐ Yes ☒ No ☐ Yes ☒ No /PETER F GODENSCHWAGER/ Examiner's Signature	☐ Met after Allowance Initials	STATE OR COUNTRY MA	SHEETS DRAWINGS 9	TOTAL CLAIMS 16	INDEPENDENT CLAIMS 1
ADDRESS DINSMORE & SHOHL LLP 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 1120	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
L1	8863	H01M4/364.CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/12/21 09:28
L2	14039	H01M4/366.CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/12/21 09:28
L3	21458	H01M4/525.CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/12/21 10:07
L4	669	"NaFeO.sub.2"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/12/21 10:07
L5	463	"alpha-NaFeO.sub.2"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/12/21 10:07
L6	66	(L4 OR L5) AND L3 AND grain boundary	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/12/21 10:07
L7	20	(L4 OR L5) AND (L1 OR L2) AND grain boundary	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/12/21 10:07
L8	37	(L4 OR L5) AND (grain boundary) AND (cathode WITH active material)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/12/21 10:07
L9	389	"alpha-NaFeO.sub.2" AND (Li OR lithium) AND (nickel OR ni) AND (oxygen OR O)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/12/21 10:36
L10	0	"alpha-NaFeO.sub.2" AND (Li OR lithium) AND (nickel OR ni) AND (oxygen OR O) AND grain boundry	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/12/21 10:36
L11	70	"alpha-NaFeO.sub.2" AND (Li OR lithium) AND (nickel OR ni) AND (oxygen OR O) AND grain boundary	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/12/21 10:36
L12	1	("9209455").DID.	US-PGPUB; USPAT	ADJ	ON	2015/12/21 10:55

EAST Search History (Interference)

< This search history is empty >

12/ 21/ 2015 11:06:23 AM

C:\ Users\ pgodenschwager\ Documents\ EAST\ Workspaces\ 14_238643.wsp

Search Notes 	Application/Control No. 14865805	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	12/21/2015	PFG

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

SEARCH NOTES		
Search Notes	Date	Examiner
inventor name search (PALM)	12/21/2015	PFG
EAST search (see attached)	12/21/2015	PFG

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner

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

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

**DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN
APPLICATION DATA SHEET (37 CFR 1.76)****Title of
Invention**POLYCRYSTALLING METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND
ARTICLES COMPRISING THE SAME

As the below named inventor, I hereby declare that:

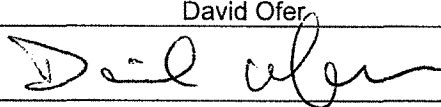
This declaration ☐ The attached application, or
is directed to:☒ United States application or PCT international application number 14/865,805
filed on 09/25/2015

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001
by fine or imprisonment of not more than five (5) years, or both.**WARNING:**

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTORInventor: David Ofer Date (Optional): _____Signature: 

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

**DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN
APPLICATION DATA SHEET (37 CFR 1.76)**

**Title of
Invention**

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

As the below named inventor, I hereby declare that:

This declaration ☐ The attached application, or
is directed to:

☒ United States application or PCT international application number 14/865,805
filed on 09/25/2015

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001
by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Adrian W. Bullen

Date (Optional) : _____

Signature: _____

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

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

**DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN
APPLICATION DATA SHEET (37 CFR 1.76)**

Title of
Invention

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

As the below named inventor, I hereby declare that:

This declaration
is directed to:

☐

The attached application, or

☒

United States application or PCT international application number

14/865,805

filed on

09/25/2015

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Suresh Sriramulu

Date (Optional): 11/03/2015

Signature:



Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

Electronic Acknowledgement Receipt

EFS ID:	24012934
Application Number:	14865805
International Application Number:	
Confirmation Number:	1076
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-10103/57
Receipt Date:	06-NOV-2015
Filing Date:	25-SEP-2015
Time Stamp:	15:48:49
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no
------------------------	----

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Oath or Declaration filed	doc00408020151106154634.pdf	232362 568a5a0e6bda7bd972e92394ab4b810f5f072768	no	3

Warnings:

Information:

Total Files Size (in bytes):

232362

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

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

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY. DOCKET NO	TOT CLAIMS	IND CLAIMS
14/865,805	09/25/2015	1722	1120	TIA-10103/57	16	1

CONFIRMATION NO. 1076

FILING RECEIPT



0000000077984432

25006
DINSMORE & SHOHL LLP
PO BOX 7021
TROY, MI 48007-7021

Date Mailed: 10/09/2015

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 Sriramulu, Arlington, MA;

Applicant(s)

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 DIV of 14/238,643 02/12/2014
which 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: 10/08/2015

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 14/865,805**

Projected Publication Date: 01/14/2016

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

430

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

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at <http://www.uspto.gov/web/offices/pac/doc/general/index.html>.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, <http://www.stopfakes.gov>. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER
Title 35, United States Code, Section 184
Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign Assets Control, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

SelectUSA

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop technology, manufacture products, deliver services, and grow your business, visit <http://www.SelectUSA.gov> or call +1-202-482-6800.



UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
14/865,805	09/25/2015	David Ofer	TIA-10103/57

CONFIRMATION NO. 1076

INFORMAL NOTICE



25006
DINSMORE & SHOHL LLP
PO BOX 7021
TROY, MI 48007-7021

Date Mailed: 10/09/2015

INFORMATIONAL NOTICE TO APPLICANT

Applicant is notified that the above-identified application contains the deficiencies noted below. No period for reply is set forth in this notice for correction of these deficiencies. However, if a deficiency relates to the inventor's oath or declaration, the applicant must file an oath or declaration in compliance with 37 CFR 1.63, or a substitute statement in compliance with 37 CFR 1.64, executed by or with respect to each actual inventor no later than the expiration of the time period set in the "Notice of Allowability" to avoid abandonment. See 37 CFR 1.53(f).

The item(s) indicated below are also required and should be submitted with any reply to this notice to avoid further processing delays.

A new inventor's oath or declaration that identifies this application (e.g., by Application Number and filing date) is required. The inventor's oath or declaration does not comply with 37 CFR 1.63 in that it:

- does not state that the above-identified application was made or authorized to be made by the person executing the oath or declaration.

David Ofer
Adrian W. Pullen
Suresh Sriramulu

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

/llvuong/

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875						Application or Docket Number 14/865,805	
APPLICATION AS FILED - PART I							
(Column 1)		(Column 2)		SMALL ENTITY		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	70		N/A	
SEARCH FEE (37 CFR 1.16(k), (l), or (m))	N/A	N/A	N/A	300		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))	20	minus 20 = *	x 40 =	0.00	OR		
INDEPENDENT CLAIMS (37 CFR 1.16(h))	1	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))				390			
			TOTAL	1120		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	
AMENDMENT A	CLAIMS REMAINING AFTER AMENDMENT	HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE(\$)	ADDITIONAL FEE(\$)		RATE(\$)
	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	
AMENDMENT B	CLAIMS REMAINING AFTER AMENDMENT	HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE(\$)	ADDITIONAL FEE(\$)		RATE(\$)
	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 14865805		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		Indep	Depend	Indep	Depend	Indep	Depend
1	1												
2		1											
3		1											
4		1											
5		1											
6		1											
7		1											
8		2											
9		2											
10		1											
11		(1)											
12		(1)											
13		2											
14		2											
15		1											
16		1											
17													
18													
19													
20													
21													
22													
23													
24													
25													
26													
27													
28													
29													
30													
31													
32													
33													
34													
35													
36													
37													
38													
39													
40													
41													
42													
43													
44													
45													
46													
47													
48													
49													
50													
Total Indep	1		0		0								
Total Depend	19	↙	0	↙	0	↙							
Total Claims	20		0		0								

51						
52						
53						
54						
55						
56						
57						
58						
59						
60						
61						
62						
63						
64						
65						
66						
67						
68						
69						
70						
71						
72						
73						
74						
75						
76						
77						
78						
79						
80						
81						
82						
83						
84						
85						
86						
87						
88						
89						
90						
91						
92						
93						
94						
95						
96						
97						
98						
99						
100						

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

UTILITY PATENT APPLICATION TRANSMITTAL (Only for new nonprovisional applications under 37 CFR 1.53(b))		Attorney Docket No. TIA-10103/57	
		First Named Inventor David Ofer	
		Title POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME	
		Express Mail Label No. _____	

APPLICATION ELEMENTS See MPEP chapter 600 concerning utility patent application contents.	ADDRESS TO: Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450
--	---

1. ☒ Fee Transmittal Form (PTO/SB/17 or equivalent) 2. ☒ Applicant asserts small entity status. See 37 CFR 1.27 3. ☐ Applicant certifies micro entity status. See 37 CFR 1.29. Applicant must attach form PTO/SB/15A or B or equivalent. 4. ☒ Specification [Total Pages <u>30</u>] Both the claims and abstract must start on a new page. (See MPEP § 608.01(a) for information on the preferred arrangement) 5. ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets <u>9</u>] 6. Inventor's Oath or Declaration [Total Pages <u>4</u>] (including substitute statements under 37 CFR 1.64 and assignments serving as an oath or declaration under 37 CFR 1.63(e)) a. ☐ Newly executed (original or copy) b. ☒ A copy from a prior application (37 CFR 1.63(d)) 7. ☒ Application Data Sheet * See note below. See 37 CFR 1.76 (PTO/AIA/14 or equivalent) 8. CD-ROM or CD-R in duplicate, large table, or Computer Program (Appendix) ☐ Landscape Table on CD 9. Nucleotide and/or Amino Acid Sequence Submission (if applicable, items a. – c. are required) a. ☐ Computer Readable Form (CRF) b. ☐ Specification Sequence Listing on: i. ☐ CD-ROM or CD-R (2 copies); or ii. ☐ Paper c. ☐ Statements verifying identity of above copies	ACCOMPANYING APPLICATION PAPERS 10. ☐ Assignment Papers (cover sheet & document(s)) Name of Assignee 11. ☐ 37 CFR 3.73(c) Statement (when there is an assignee) ☒ Power of Attorney 12. ☐ English Translation Document (if applicable) 13. ☐ Information Disclosure Statement (PTO/SB/08 or PTO-1449) ☐ Copies of citations attached 14. ☐ Preliminary Amendment 15. ☐ Return Receipt Postcard (MPEP § 503) (Should be specifically itemized) 16. ☐ Certified Copy of Priority Document(s) (if foreign priority is claimed) 17. ☐ Nonpublication Request Under 35 U.S.C. 122(b)(2)(B)(i). Applicant must attach form PTO/SB/35 or equivalent. 18. ☐ Other:
--	---

***Note:** (1) Benefit claims under 37 CFR 1.78 and foreign priority claims under 1.55 must be included in an Application Data Sheet (ADS).
 (2) For applications filed under 35 U.S.C. 111, the application must contain an ADS specifying the applicant if the applicant is an assignee, person to whom the inventor is under an obligation to assign, or person who otherwise shows sufficient proprietary interest in the matter. See 37 CFR 1.46(b).

19. CORRESPONDENCE ADDRESS			
☒ The address associated with Customer Number: <u>25006</u> OR ☐ Correspondence address below			
Name _____			
Address _____			
City	State	Zip Code	
Country	Telephone	Email	

Signature	/Weston R. Gould, Ph. D./	Date	September 25, 2015
Name (Print/Type)	Weston R. Gould, Ph. D.	Registration No. (Attorney/Agent)	59,142

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

FEE TRANSMITTAL		Complete if known		
		Application Number	Not Yet Assigned	
		Filing Date		
		First Named Inventor	David Ofer	
☒ Applicant asserts small entity status. See 37 CFR 1.27.		Examiner Name	Not Yet Assigned	
☐ 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.		Art Unit	N/A	
TOTAL AMOUNT OF PAYMENT	(\$)	1,120.00	Practitioner Docket No.	TIA-10103/57

METHOD OF PAYMENT (check all that apply)

☐ Check ☒ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): _____
☐ Deposit Account Deposit Account Number: 04-1133 Deposit Account Name: Dinsmore & Shohl LLP

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	730.00
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	Extra Claims	Fee (\$)	Fee Paid (\$)
16	- 20 or HP =	x	=
HP = highest number of total claims paid for, if greater than 20.			
Indep. Claims	Extra Claims	Fee (\$)	Fee Paid (\$)
2	- 3 or HP =	x	=
HP = highest number of independent claims paid for, if greater than 3.			
		Multiple Dependent Claims	
		Fee (\$)	Fee Paid (\$)
		390.00	390.00

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 (\$)
30	- 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):

SUBMITTED BY			
Signature	Weston R. Gould, Ph. D./	Registration No. (Attorney/Agent)	59,142
Telephone	(248) 647-6000		
Name (Print/Type)	Weston R. Gould, Ph. D.	Date	September 25, 2015

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

UTILITY PATENT APPLICATION TRANSMITTAL		Attorney Docket No. TIA-10103/57	
		First Named Inventor David Ofer	
(Only for new nonprovisional applications under 37 CFR 1.53(b))		Title POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME	
		Express Mail Label No.	

APPLICATION ELEMENTS See MPEP chapter 600 concerning utility patent application contents.	ADDRESS TO: Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450
---	---

1. ☒ Fee Transmittal Form (PTO/SB/17 or equivalent) 2. ☒ Applicant asserts small entity status. See 37 CFR 1.27 3. ☐ Applicant certifies micro entity status. See 37 CFR 1.29. Applicant must attach form PTO/SB/15A or B or equivalent. 4. ☒ Specification [Total Pages <u>30</u>] Both the claims and abstract must start on a new page. (See MPEP § 608.01(a) for information on the preferred arrangement) 5. ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets <u>9</u>] 6. Inventor's Oath or Declaration [Total Pages <u>4</u>] (including substitute statements under 37 CFR 1.64 and assignments serving as an oath or declaration under 37 CFR 1.63(e)) a. ☐ Newly executed (original or copy) b. ☒ A copy from a prior application (37 CFR 1.63(d)) 7. ☒ Application Data Sheet * See note below. See 37 CFR 1.76 (PTO/AIA/14 or equivalent) 8. CD-ROM or CD-R in duplicate, large table, or Computer Program (Appendix) ☐ Landscape Table on CD 9. Nucleotide and/or Amino Acid Sequence Submission (if applicable, items a. – c. are required) a. ☐ Computer Readable Form (CRF) b. ☐ Specification Sequence Listing on: i. ☐ CD-ROM or CD-R (2 copies); or ii. ☐ Paper c. ☐ Statements verifying identity of above copies	ACCOMPANYING APPLICATION PAPERS 10. ☐ Assignment Papers (cover sheet & document(s)) Name of Assignee 11. ☐ 37 CFR 3.73(c) Statement (when there is an assignee) ☒ Power of Attorney 12. ☐ English Translation Document (if applicable) 13. ☐ Information Disclosure Statement (PTO/SB/08 or PTO-1449) ☐ Copies of citations attached 14. ☐ Preliminary Amendment 15. ☐ Return Receipt Postcard (MPEP § 503) (Should be specifically itemized) 16. ☐ Certified Copy of Priority Document(s) (if foreign priority is claimed) 17. ☐ Nonpublication Request Under 35 U.S.C. 122(b)(2)(B)(i). Applicant must attach form PTO/SB/35 or equivalent. 18. ☐ Other:
--	--

***Note:** (1) Benefit claims under 37 CFR 1.78 and foreign priority claims under 1.55 must be included in an Application Data Sheet (ADS).
 (2) For applications filed under 35 U.S.C. 111, the application must contain an ADS specifying the applicant if the applicant is an assignee, person to whom the inventor is under an obligation to assign, or person who otherwise shows sufficient proprietary interest in the matter. See 37 CFR 1.46(b).

19. CORRESPONDENCE ADDRESS			
☒ The address associated with Customer Number: <u>25006</u> OR ☐ Correspondence address below			
Name			
Address			
City	State	Zip Code	
Country	Telephone	Email	

Signature	/Weston R. Gould, Ph. D./	Date	September 25, 2015
Name (Print/Type)	Weston R. Gould, Ph. D.	Registration No. (Attorney/Agent)	59,142

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

FEE TRANSMITTAL		Complete if known		
		Application Number	Not Yet Assigned	
		Filing Date		
		First Named Inventor	David Ofer	
☒ Applicant asserts small entity status. See 37 CFR 1.27.		Examiner Name	Not Yet Assigned	
☐ 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.		Art Unit	N/A	
TOTAL AMOUNT OF PAYMENT	(\$)	1,120.00	Practitioner Docket No.	TIA-10103/57

METHOD OF PAYMENT (check all that apply)

☐ Check ☒ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): _____
☐ Deposit Account Deposit Account Number: 04-1133 Deposit Account Name: Dinsmore & Shohl LLP

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	730.00
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			
<u>16</u> - 20 or HP = _____ x _____ = _____			
HP = highest number of total claims paid for, if greater than 20.			
Indep. Claims			
<u>2</u> - 3 or HP = _____ x _____ = _____			
HP = highest number of independent claims paid for, if greater than 3.			
	Fee Paid (\$)	Fee Paid (\$)	Fee Paid (\$)
		390.00	390.00

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 (\$)
<u>30</u>	- 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): _____

SUBMITTED BY

Signature	Weston R. Gould, Ph. D./	Registration No. (Attorney/Agent)	59,142	Telephone	(248) 647-6000
Name (Print/Type)	Weston R. Gould, Ph. D.	Date	September 25, 2015		

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-10103/57
		Application Number	
Title of Invention	POLYCRYSTALLINE 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.)
--------------------------	---

Inventor Information:

Inventor 1					Remove		
Legal Name							
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	
Mailing Address of Inventor:							
Address 1		37 Booth Street					
Address 2							
City	Needham			State/Province	MA		
Postal Code	02494			Country i	US		
Inventor 2					Remove		
Legal Name							
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	
Mailing Address of Inventor:							
Address 1		35 Boylston Street, #3					
Address 2							
City	Boston			State/Province	MA		
Postal Code	02130			Country i	US		
Inventor 3					Remove		
Legal Name							
Prefix	Given Name		Middle Name		Family Name		Suffix
Mr.	Suresh				Sriramulu		
Residence Information (Select One) ☒ US Residency ☐ Non US Residency ☐ Active US Military Service							

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-10103/57	
		Application Number		
Title of Invention	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME			

City	Arlington	State/Province	MA	Country of Residence	US
------	-----------	----------------	----	----------------------	----

Mailing Address of Inventor:

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.					

Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below. For further information see 37 CFR 1.33(a).			
☐ An Address is being provided for the correspondence Information of this application.			
Customer Number	25006		
Email Address		Add Email	Remove Email

Application Information:

Title of the Invention	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME		
Attorney Docket Number	TIA-10103/57	Small Entity Status Claimed	☒
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	9	Suggested Figure for Publication (if any)	

Filing By Reference :

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)
☐ Request Not to Publish. I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application has not and will not be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

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-10103/57
		Application Number	
Title of Invention	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME		

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32). Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:			
☒	Customer Number	☐	US Patent Practitioner
☐	Limited Recognition (37 CFR 11.9)		
Customer Number	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, 365(c), or 386(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.

When referring to the current application, please leave the application number blank.

Prior Application Status	Pending	Remove	
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
	Division of	14238643	2014-02-12
Prior Application Status		Remove	
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
14238643	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	Claims benefit of provisional	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 priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)ⁱ the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove			
Application Number	Country ⁱ	Filing Date (YYYY-MM-DD)	Access Code ^j (if applicable)

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-10103/57
		Application Number	
Title of Invention	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME		

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

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.

NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Authorization to Permit Access:

☐ Authorization to Permit Access to the Instant Application by the Participating Offices

If checked, the undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the World Intellectual Property Office (WIPO), and any other intellectual property offices in which a foreign application claiming priority to the instant patent application is filed access to the instant patent application. See 37 CFR 1.14(c) and (h). This box should not be checked if the applicant does not wish the EPO, JPO, KIPO, WIPO, or other intellectual property office in which a foreign application claiming priority to the instant patent application is filed to have access to the instant patent application.

In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the instant patent application with respect to: 1) the instant patent application-as-filed; 2) any foreign application to which the instant patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the instant patent application; and 3) any U.S. application-as-filed from which benefit is sought in the instant patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date of filing this Authorization.

Applicant Information:

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

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-10103/57
		Application Number	
Title of Invention	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME		

Applicant 1			
If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.			
Clear			
☒ Assignee		☐ Legal Representative under 35 U.S.C. 117	
		☐ Joint Inventor	
☐ Person to whom the inventor is obligated to assign.		☐ Person who shows sufficient proprietary interest	
If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:			
Name of the Deceased or Legally Incapacitated Inventor :			
If the Applicant is an Organization check here. ☒			
Organization Name	TIAX LLC		
Mailing Address Information For Applicant:			
Address 1	35 Hartwell Avenue		
Address 2			
City	Lexington	State/Province	MA
Country	US	Postal Code	02421-3102
Phone Number		Fax Number	
Email Address			
Additional Applicant Data may be generated within this form by selecting the Add button.			

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.	
Assignee 1	
Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.	
If the Assignee or Non-Applicant Assignee is an Organization check here. ☐	

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-10103/57
		Application Number	
Title of Invention	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME		

Prefix	Given Name	Middle Name	Family Name	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		State/Province	
Country i		Postal Code	
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button.

Signature:

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications.					
Signature	/Weston R. Gould, Ph. D./			Date (YYYY-MM-DD)	2015-09-25
First Name	Weston	Last Name	Gould, Ph. D.	Registration Number	59142
Additional Signature may be generated within this form by selecting the Add button.					

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.**

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 the Freedom of Information Act requires disclosure of these records.
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 inspections 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.

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:

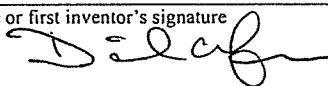
☒ no such U.S./PCT applications have been filed.

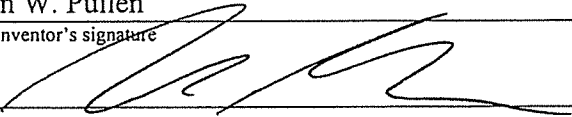
☐ such U.S./PCT applications have been filed as follows:

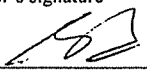
Application Number	Relationship	Parent Application	Date of Filing

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

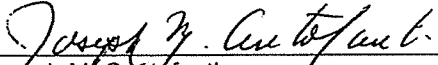
Assignee Name and Address:

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		

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

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a divisional of U.S. Application No: 14,238,643, filed February 12, 2014, which is a U.S. National Phase of Application No: PCT/US2012/048602, filed July 27, 2012, and which claims priority to U.S. Provisional Application No. 61/575,115, filed on August 16, 2011, the entire contents of each of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

(1) FIELD OF THE INVENTION

[0002] Disclosed is a polycrystalline metal oxide, methods of manufacture thereof, and articles comprising the same.

(2) DESCRIPTION OF THE RELATED ART

[0003] 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.

[0004] 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 OF THE INVENTION

[0005] 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.

[0006] 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.

[0007] Also disclosed is a lithium-ion battery including at least one of the foregoing particles.

[0008] 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

[0009] 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:

[0010] FIG. 1 is a schematic perspective view of an embodiment of a cross-section of a secondary particle;

[0011] FIG. 2 is a schematic illustration of an embodiment of a battery;

[0012] FIG. 3 is a scanning electron micrograph (SEM) of a thin cross-section of a secondary particle prepared in Example 2;

[0013] FIG. 4 is an enlarged view of the secondary particle of FIG. 3 showing the location of EDX spot analyses;

[0014] FIG. 5 is a further enlarged view of the secondary particle of FIG. 3 showing the location of EDX spot analyses;

[0015] 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;

[0016] 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;

[0017] 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;

[0018] FIG. 9 is a scanning transmission electron micrograph (STEM) of a thin cross-section of a secondary particle prepared in Example 6;

[0019] FIG. 10 is an enlarged view of area A indicated in FIG. 9;

[0020] 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;

[0021] FIG. 12 is a Ni EDX map of area A indicated in FIG. 9; and

[0022] FIG. 13 is a Co EDX map of area A indicated in FIG. 9.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0023] 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.

[0024] 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.

[0025] 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.

[0026] 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.

[0027] 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.

[0028] 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.

[0029] 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.

[0030] 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.

[0031] 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.

[0032] 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.

[0033] 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 0.08 mole, per mole of the first composition, is specifically mentioned.

[0034] 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.

[0035] 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.

[0036] 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.

[0037] 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.

[0038] 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.

[0039] 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.

[0040] 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.

[0041] 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.

[0042] 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.

[0043] 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.

[0044] 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.

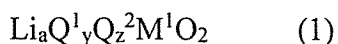
[0045] In an embodiment, the second composition of the grain boundaries comprises lithium in an amount of about 0.1 to about 1.3 moles, specifically about 0.2 to about 1.2 moles, more specifically about 0.3 to about 1.1 moles, per mole of the second composition; nickel in an amount of about 0.1 to about 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.

[0046] 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.

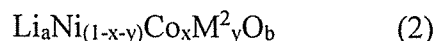
[0047] The additional metal of the second composition may comprise Mg, Sr, Ca, Cu, Zn, Mn, Al, V, Ba, Zr, Ti, Cr, Fe, Mo, B, or a combination thereof. In an embodiment, the additional metal of the second composition comprises Mg, Al, V, Ti, B, Zr, or Mn, or a combination thereof. In another embodiment, 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.

[0048] In an embodiment, the first and second compositions may each independently comprise a composition of Formula 1:



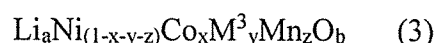
wherein Q^1 is Mg, Sr, Ca, Cu, Zn, or a combination thereof, Q^2 is Mn, Al, Mg, Ca, Sr, Ba, Zn, Ti, Zr, Cr, Mo, Fe, V, Si, Ga, B, or a combination thereof, M^1 is Ni and Co, $0.1 \leq a \leq 1.2$, $0 < y \leq 0.2$, and $0 \leq z \leq 0.6$, with the proviso that the concentration of cobalt in the second 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 $0.05 < y \leq 0.1$.

[0049] In an embodiment, the first and second compositions may each independently comprise a composition of Formula 2:



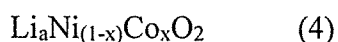
wherein M^2 is Al, V, Ti, B, Zr, Mn, or a combination thereof, $0.1 \leq a \leq 1.3$, $0.01 \leq x \leq 0.5$, $0 < y \leq 0.2$, and $1.7 \leq b \leq 2.3$, provided that x in the second composition is greater than x in the first composition. In an embodiment M^2 is Al, V, Ti, B, Zr, or Mn. An embodiment 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 $0.05 < y \leq 0.1$.

[0050] 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 $1.9 \leq b \leq 2.1$.

[0051] 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 $0.3 < x < 0.4$.

[0052] 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 $0.2 < x < 0.5$.

[0053] 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.

[0054] 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.

[0055] 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.

[0056] 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.

[0057] 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.

[0058] 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.

[0059] 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.

[0060] 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 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.

[0061] 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.

[0062] 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.

[0063] The battery may have any suitable configuration or shape, and may be cylindrical or prismatic.

[0064] 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 $\alpha\text{-NaFeO}_2$ -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.

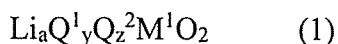
[0065] The above observations indicate that Co substitution in lithium nickel oxides having the layered α -NaFeO₂-type structure enhances electrochemical performance by stabilizing the grain boundaries of the secondary particle. Therefore Co-substituted lithium nickel oxides with Co preferentially disposed 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.

[0066] 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 LiCoO₂, to provide a LiCoO₂ coated LiNi_(1-x)Co_xO₂ 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.

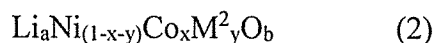
[0067] In an embodiment disclosed is a particle, comprising: a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition, nickel in an amount of about 0.1 to 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.

[0068] 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:



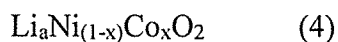
wherein Q^1 is Mg, Sr, Ca, Cu, Zn, or a combination thereof, Q^2 is Mn, Al, Mg, Ca, Sr, Ba, Zn, Ti, Zr, Cr, Mo, Fe, V, Si, Ga, or B, or a combination thereof, M^1 is Ni and Co, $0.1 \leq a \leq 1.2$, $0 < y \leq 0.2$, and $0 \leq z \leq 0.6$; and/or (xvii) the first and second compositions each independently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

[0069] Also disclosed is 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.

[0070] Also disclosed is an electrode for a lithium-ion battery, the electrode comprising the particle, and a lithium-ion battery comprising the particle.

[0071] 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 -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.

[0072] The disclosed embodiment is further illustrated in the following Examples.

EXAMPLES

Example 1. Preparation of $\text{Li}_{1.05}\text{Mg}_{0.025}\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}_{2.05}$

[0073] 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 $\text{Li}(\text{OH})_2$ (anhydrous fine powder available from Sigma-Aldrich, Inc., St. Louis, Mo.), 14.8 g $\text{Mg}(\text{OH})_2$ (fine powder available from Alfa Aesar, Ward Hill, Mass.), and 35.0 g LiNO_3 (crystals available from Alfa Aesar, Ward Hill, Mass.). To the mixture of $\text{Li}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, and LiNO_3 was added 940.3 g $\text{Ni}_{0.92}\text{Co}_{0.08}(\text{OH})_2$ (available from OM Group, Inc.) in a 1 liter jar. The compounds were mixed by shaking the jar.

[0074] 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.

[0075] 0.3 grams (g) of LiNO_3 and 117.4 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 1000 g of H_2O 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 $c=14.192 \text{ \AA}$.

[0076] 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.

[0077] FIG. 3 is a low-resolution STEM image of secondary particle having a diameter of about 7 μm . The secondary particle is comprised of densely agglomerated primary crystallites.

[0078] 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.

[0079] 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.

[0080] 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

[0081] 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 α - 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

[0082] 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 LiPF₆ 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%

[0083] 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.

[0084] 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 LiPF₆ 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 Li_{1.05}Mg_{0.025}NiO_{2.05}.

[0085] A material having the composition Li_{1.05}Mg_{0.025}NiO_{2.05} was prepared using the same method as provided in Example 1, except that 940.3 g of Ni(OH)₂ (#543 high density spherical powder available from OM Group, Inc., Cleveland, Ohio) was used in place of Ni_{0.92}Co_{0.08}(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.

[0086] 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 α - 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.

[0087] 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.

[0088] 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.

[0089] 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.

[0090] 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.

[0091] 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

CLAIMS

1. A particle, comprising:
 - a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising:
 - lithium, nickel, and oxygen;
 - 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 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. 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. 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. 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 1 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 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. The particle of claims 1 or 7, wherein the first composition further contains cobalt, with the cobalt concentration in the range of 0 to about 0.5 mole per mole of the first composition.

9. The particle of claim 8 wherein the first composition further contains cobalt, with the cobalt concentration in the range of 0.0 to about 0.3 mole per mole of the first composition

10. 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.

11. The particle of claim 1, 7, or 9, wherein said first composition comprises nickel at a concentration of 0.8 to 1 moles per mole of said first composition.

12. The particle of claim 11 wherein said first composition comprises nickel at a concentration of 0.92 moles per mole of said first composition.

13. The particle of claims 1 or 7 wherein the first composition comprises:
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 0.99 mole, per mole of the first composition;
and
cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition.

14. The particle of claims 1 or 7 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.

15. 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, Li, Al, Ti, B, or Si, or a combination thereof.

16. A method of manufacturing the particle of claim 1, 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; 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.

ABSTRACT OF THE DISCLOSURE

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.

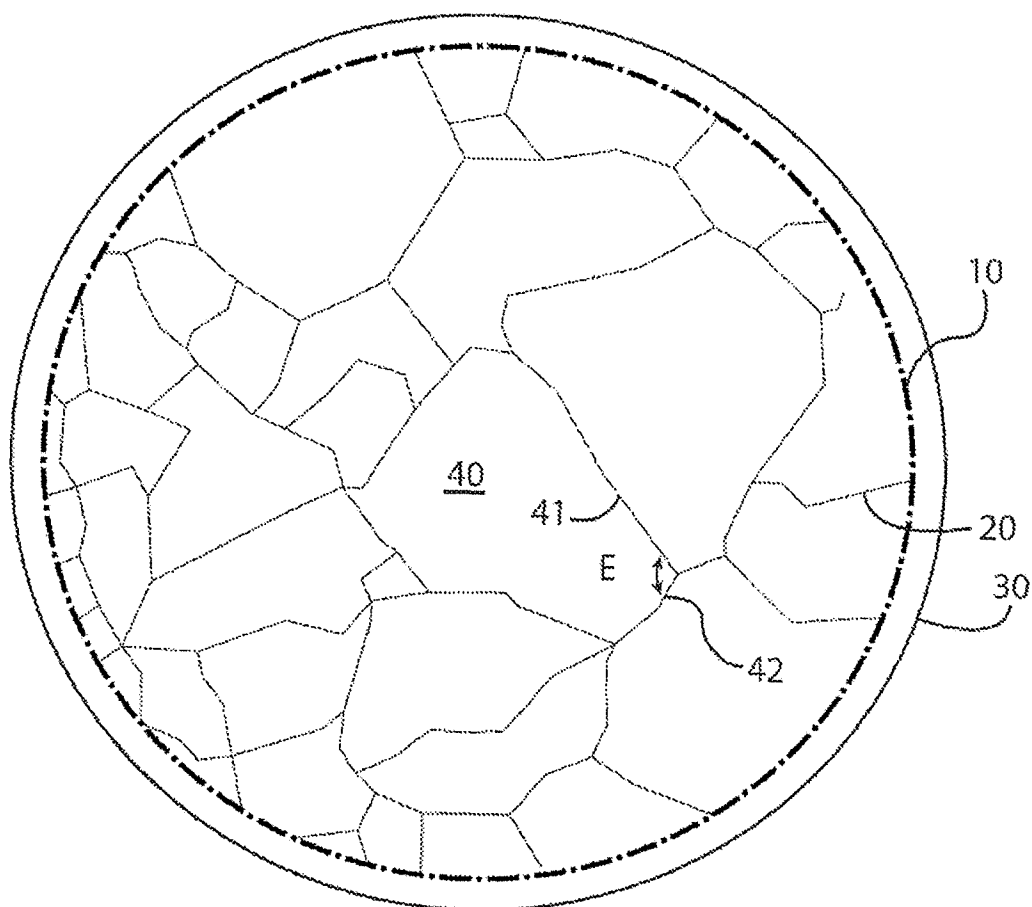


FIG. 1

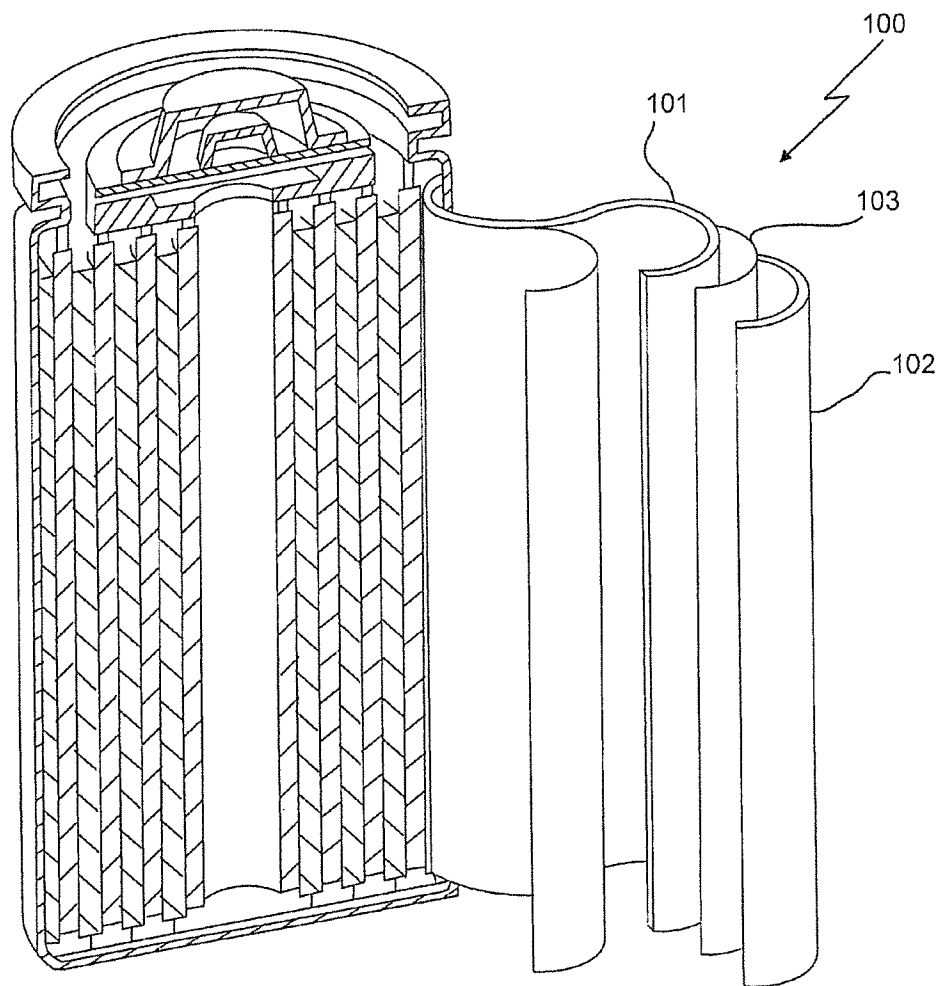


FIG. 2

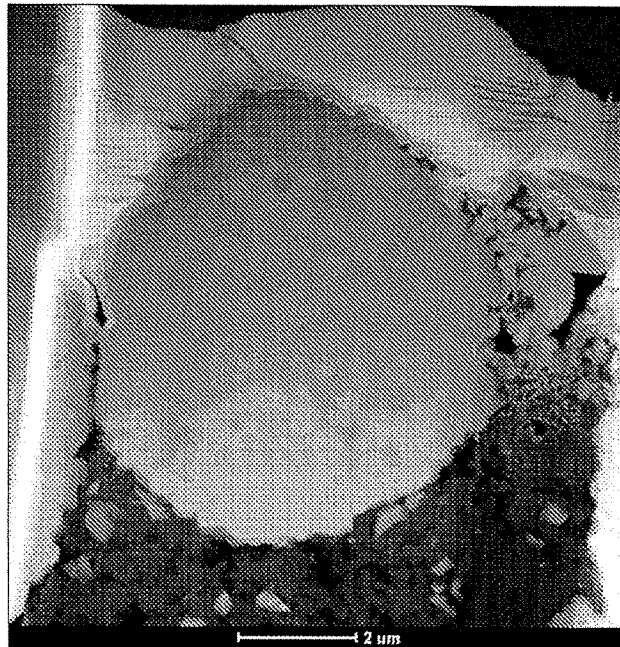


FIG. 3

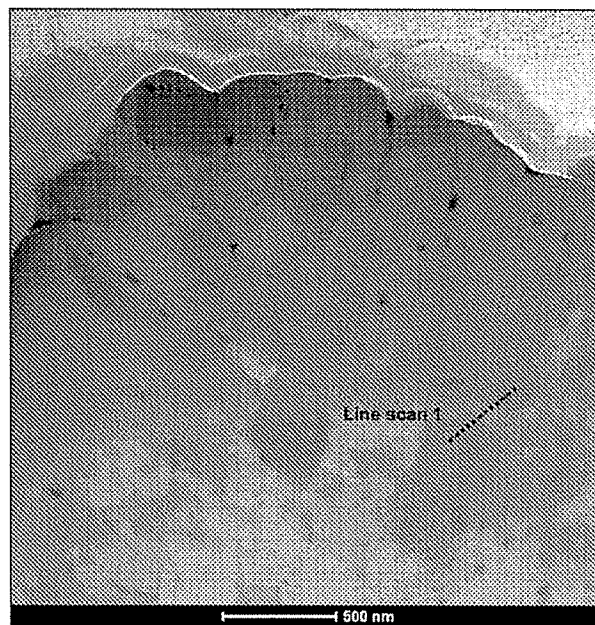


FIG. 4

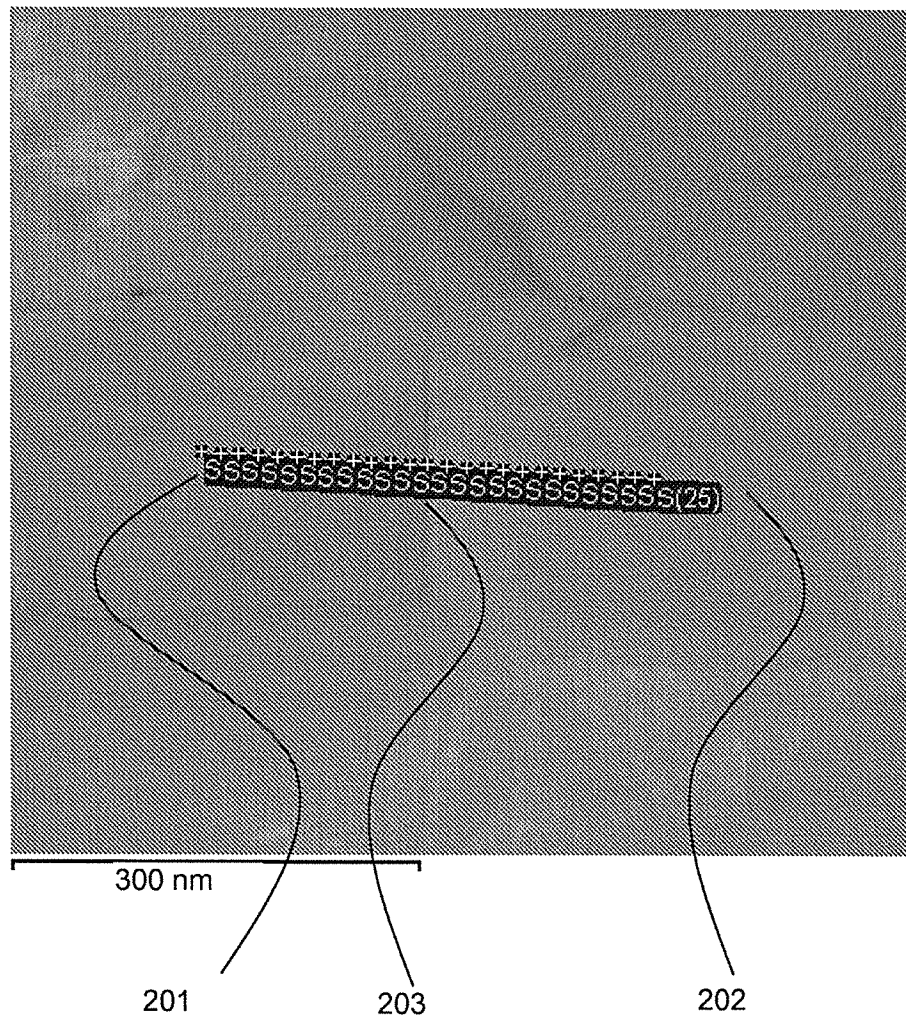


FIG. 5

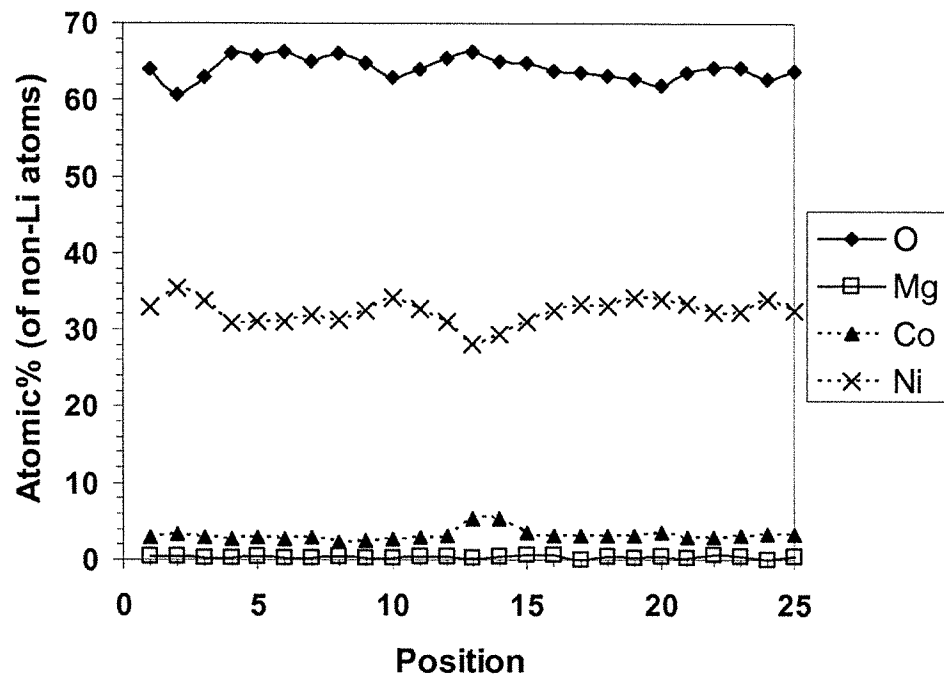


FIG. 6

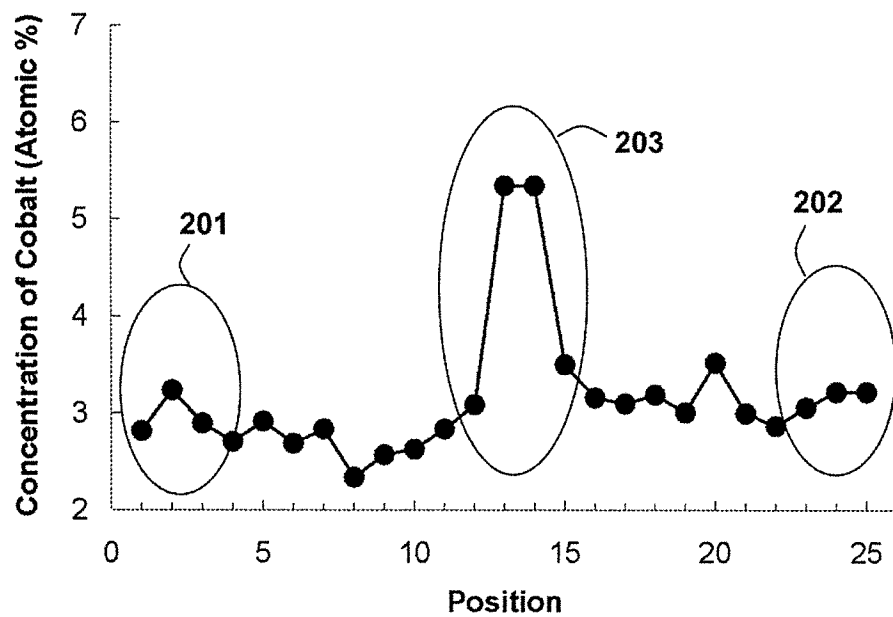


FIG. 7

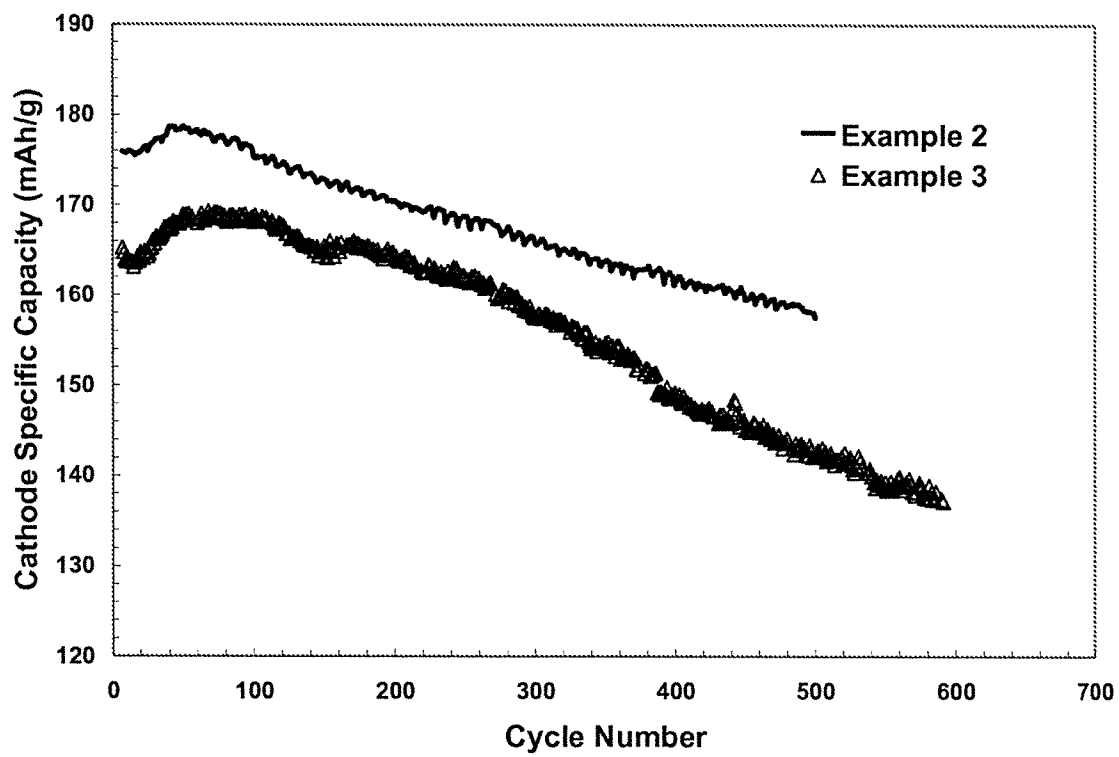


FIG. 8

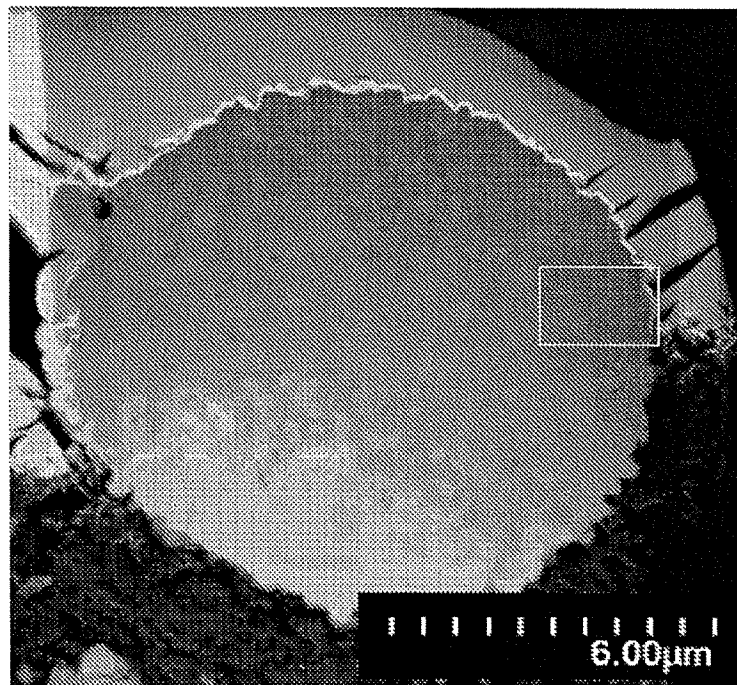


FIG. 9

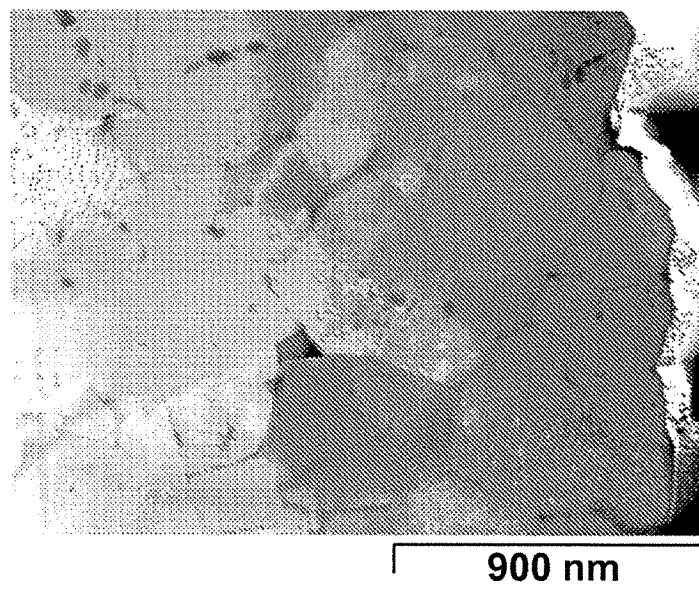


FIG. 10

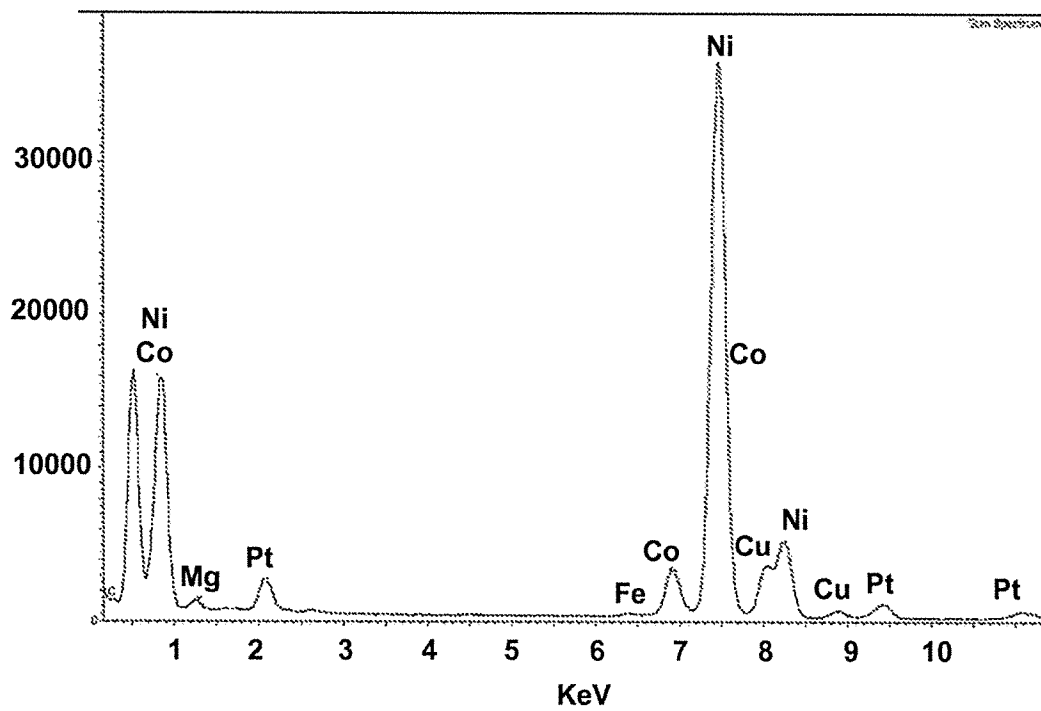


FIG. 11

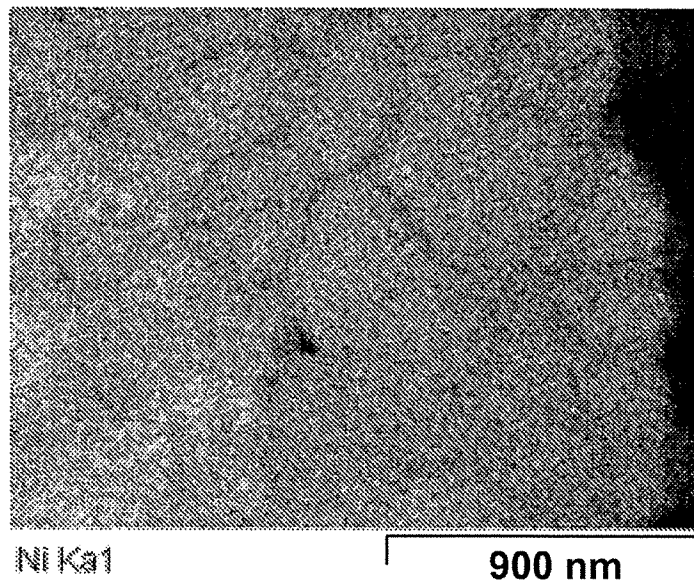


FIG. 12

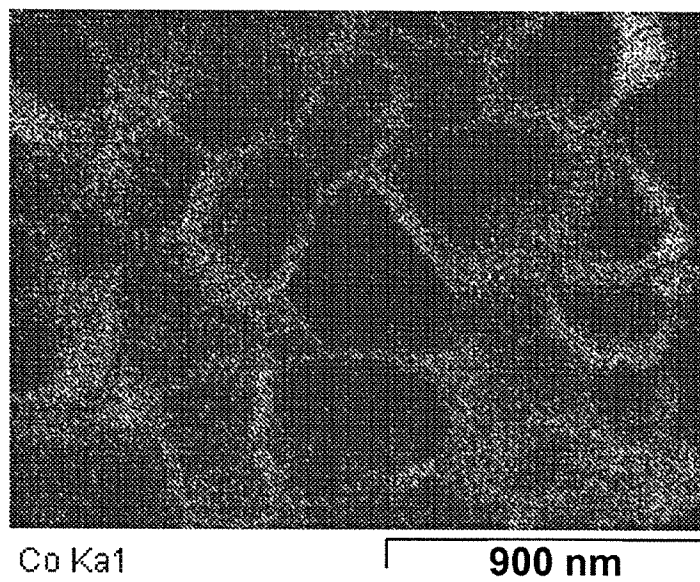


FIG. 13

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:	TIA-10103/57			
Filed as Small Entity				
Filing Fees for Utility under 35 USC 111(a)				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Utility filing Fee (Electronic filing)	4011	1	70	70
Utility Search Fee	2111	1	300	300
Utility Examination Fee	2311	1	360	360
Pages:				
Claims:				
Multiple Dependent Claims	2203	1	390	390
Miscellaneous-Filing:				
Petition:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
Total in USD (\$)				1120

Electronic Acknowledgement Receipt

EFS ID:	23608641
Application Number:	14865805
International Application Number:	
Confirmation Number:	1076
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-10103/57
Receipt Date:	25-SEP-2015
Filing Date:	
Time Stamp:	15:42:18
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	\$ 1120
RAM confirmation Number	2494
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		doc00236920150925144638.pdf	4194649	yes	53
			a6bde5be6401e7126b9c0071a119e85a997a481b		
	Multipart Description/PDF files in .zip description				
	Document Description		Start		End
	Transmittal of New Application		1		1
	Miscellaneous Incoming Letter		2		2
	Application Data Sheet		3		9
	Oath or Declaration filed		10		13
	Miscellaneous Incoming Letter		14		14
	Specification		15		39
	Claims		40		43
	Abstract		44		44
	Drawings-only black and white line drawings		45		53
	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	37104	no	2
			1c24b6b141688a530126e14074391388c7667494		
Warnings:					
Information:					
Total Files Size (in bytes):			4231753		

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.