

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
20 February 2003 (20.02.2003)

PCT

(10) International Publication Number
WO 2003/015198 A3

(51) International Patent Classification⁷: **H01M 4/50**, 4/48

(21) International Application Number:
PCT/US2002/024684

(22) International Filing Date: 2 August 2002 (02.08.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/310,622 7 August 2001 (07.08.2001) US

(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3437 (US).

(72) Inventors: **DAHAN, Jeffrey, R.**; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). **LU, ZHONGHUA**; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: **WEISS, Lucy, C.** et al.; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, P.O. Box 33427, St. Paul, MN 55133-3427 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), 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 (utility model), 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, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations 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, 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, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations*

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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

1 April 2004

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.

(54) Title: CATHODE COMPOSITIONS FOR LITHIUM ION BATTERIES

(57) Abstract: A cathode composition for a lithium ion battery that contains lithium having the formula (a) $\text{Li}_x\text{y}[\text{M}^{1+}_{1-x}(1-b)\text{Mn}^{2+}_b]\text{O}_{2+2y}$ or (b) $\text{Li}_x\text{y}[\text{M}^{1+}_{1-x}(1-b)\text{Mn}^{2+}_b]\text{O}_{1.5+2y}$ where $0 \leq y < 1$, 0



WO 2003/015198 A3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/24684

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 H01M4/50 H01M4/48

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 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)

INSPEC, EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE INSPEC 'Online! INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB; PAULSEN J M ET AL: "O2 structure Li/sub 2/3/ Ni/sub 1/3/Mn/sub 2/3/O/sub 2/: a new layered cathode material for rechargeable lithium batteries. III. Ion exchange" Database accession no. 6718866 XP002259657 abstract & JOURNAL OF THE ELECTROCHEMICAL SOCIETY, AUG. 2000, ELECTROCHEM. SOC, USA, vol. 147, no. 8, pages 2862-2867, ISSN: 0013-4651 --- -/--	1-5, 13

☒ 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.

* & * document member of the same patent family

Date of the actual completion of the international search

2 February 2004

Date of mailing of the international search report

20.02.04

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

Thanos, I

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/24684

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 26683 A (UNIV ST ANDREWS ;ARMSTRONG ANTHONY ROBERT (GB); BRUCE PETER GEORGE) 24 July 1997 (1997-07-24)	2-5,13
Y	page 9, paragraph 3 -page 10, paragraph 2; claims 4,5; figures 3,5 page 2, paragraph 3 -page 3, paragraph 5 page 7, paragraph 3 ---	1-5,13
X	US 6 168 887 B1 (DAHN JEFFREY R ET AL) 2 January 2001 (2001-01-02)	2,13
Y	column 1, line 38 -column 2, line 21 column 3, line 25 -column 4, line 17 column 5, line 18 -column 6, line 57 column 10, line 22 -column 12, line 7; claims 5,16 ---	1-5,13
Y	EP 0 813 256 A (JAPAN STORAGE BATTERY CO LTD) 17 December 1997 (1997-12-17) column 5, line 32-53 column 3, line 12 -column 4, line 51 ---	1-5,13
A	US 4 780 381 A (SHACKLETTE LAWRENCE W ET AL) 25 October 1988 (1988-10-25) column 3, line 7 -column 4, line 42 ---	1,13
L	WO 02 089234 A (3M INNOVATIVE PROPERTIES CO) 7 November 2002 (2002-11-07) the whole document ---	1
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 08, 30 June 1999 (1999-06-30) & JP 11 086861 A (RES DEV CORP OF JAPAN), 30 March 1999 (1999-03-30) abstract examples 2-4; table 1 ---	6-12
X	WO 01 15252 A (SUEYOSHI TSUYOSHI ;MIYAGI HIDEKAZU (JP); MITSUBISHI CHEM CORP (JP)) 1 March 2001 (2001-03-01) example 4 ---	6-8,12

	-/--	

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/24684

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE INSPEC 'Online! INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB; PAULSEN J M ET AL: "Layered Li-Mn-oxide with the O/sub 2/ structure: a cathode material for Li-ion cells which does not convert to spinel" Database accession no. 6419232 XP002268799 abstract & JOURNAL OF THE ELECTROCHEMICAL SOCIETY, OCT. 1999, ELECTROCHEM. SOC, USA, vol. 146, no. 10, pages 3560-3565, ISSN: 0013-4651 ---	6-8
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 11, 30 September 1998 (1998-09-30) & JP 10 172571 A (AICHI STEEL WORKS LTD), 26 June 1998 (1998-06-26) page 4, paragraph 22 page 5, paragraphs 42-48 ---	6-12
X	US 5 858 324 A (ZHENG TAO ET AL) 12 January 1999 (1999-01-12) column 1, line 18 -column 3, line 15; examples 1-37 ---	11,12
X	DATABASE INSPEC 'Online! THE INSTITUTION OF ELECTRICAL ENGINEERS, STEVENAGE, GB; SA HEUM KIM ET AL: "Factors controlling the stability of O3- and P2-type layered MnO/sub 2/ structures and spinel transition tendency in Li secondary batteries" Database accession no. 6525597 XP002268800 abstract & JOURNAL OF THE ELECTROCHEMICAL SOCIETY, FEB. 2000, ELECTROCHEM. SOC, USA, vol. 147, no. 2, pages 413-419, ISSN: 0013-4651 ---	1,6
Y	abstract & JOURNAL OF THE ELECTROCHEMICAL SOCIETY, FEB. 2000, ELECTROCHEM. SOC, USA, vol. 147, no. 2, pages 413-419, ISSN: 0013-4651 ---	6-8
Y	US 6 214 493 B1 (ARMSTRONG ANTHONY ROBERT ET AL) 10 April 2001 (2001-04-10) column 4, line 49 -column 6, line 12 ---	6-8
X	US 5 753 202 A (GIONET PAUL ET AL) 19 May 1998 (1998-05-19) column 2, line 1 -column 3, line 29 --- -/--	6-8,12

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/24684

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 22, 9 March 2001 (2001-03-09) & JP 2001 143710 A (SAMSUNG SDI CO LTD), 25 May 2001 (2001-05-25) abstract -----	6-8, 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 02/24684

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

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

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

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

see additional sheet

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

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1, 2-5, 13

This first invention (claims 1, 13) concerns cathode compositions (and related batteries) comprising Li, Mn, O and metal(s) "M" based on a $\text{Li}(x)\text{Mn}(y)\text{M}(z)\text{O}(u)$ compound exhibiting a layered crystal structure, which (special technical feature) (i) crystallise in a single O3 phase and are capable of providing an energy density of 130 mAh/g after 100 full charge/discharge cycles under 30 mA/g at 30°C. The second invention grouped together with said first invention concerns cathode compositions comprising Li, Mn, O and metal(s) "M" based on a $\text{Li}(x)\text{Mn}(y)\text{M}(z)\text{O}(u)$ compound which upon electrochemical cycling (full charging - full discharging) give rise to respectively different pairs of ionic states for metal "M", in particular (as special technical feature) ionic state 2+ in the fully discharged state and ionic state 4+ in the fully charged state (this occurs when M = Ni).

2. Claims: 6-9, 12

This invention concerns cathode compositions comprising Li, Mn, O and metal(s) "M" based on a $\text{Li}(x)\text{Mn}(y)\text{M}(z)\text{O}(u)$ compound which upon electrochemical cycling (full charging - full discharging) give rise to respectively different pairs of ionic states for metal "M", in particular (as special technical feature) ionic state 3+ in the fully discharged state and ionic state 4+ in the fully charged state.

3. Claims: 10, 11

This invention concerns cathode compositions comprising Li, Mn, O and metal(s) "M" based on a $\text{Li}(x)\text{Mn}(y)\text{M}(z)\text{O}(u)$ compound which upon electrochemical cycling (full charging - full discharging) give rise to respectively different pairs of ionic states for metal "M", in particular (as special technical feature) ionic state 3+ in the fully discharged state and ionic state 6+ in the fully charged state.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/24684

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9726683	A	24-07-1997	AU 713144 B2 AU 1387597 A CA 2242901 A1 EP 0875080 A1 WO 9726683 A1 JP 2000503453 T US 6214493 B1	25-11-1999 11-08-1997 24-07-1997 04-11-1998 24-07-1997 21-03-2000 10-04-2001
US 6168887	B1	02-01-2001	NONE	
EP 0813256	A	17-12-1997	JP 10003921 A CN 1171638 A ,B DE 69712409 D1 DE 69712409 T2 EP 0813256 A2 US 5981106 A	06-01-1998 28-01-1998 13-06-2002 03-04-2003 17-12-1997 09-11-1999
US 4780381	A	25-10-1988	NONE	
WO 02089234	A	07-11-2002	US 2003027048 A1 WO 02089234 A1	06-02-2003 07-11-2002
JP 11086861	A	30-03-1999	NONE	
WO 0115252	A	01-03-2001	WO 0115252 A1 JP 2001126731 A JP 2001261341 A JP 2001261342 A	01-03-2001 11-05-2001 26-09-2001 26-09-2001
JP 10172571	A	26-06-1998	NONE	
US 5858324	A	12-01-1999	AU 6462098 A JP 2001520617 T WO 9846528 A1	11-11-1998 30-10-2001 22-10-1998
US 6214493	B1	10-04-2001	AU 713144 B2 AU 1387597 A CA 2242901 A1 EP 0875080 A1 WO 9726683 A1 JP 2000503453 T	25-11-1999 11-08-1997 24-07-1997 04-11-1998 24-07-1997 21-03-2000
US 5753202	A	19-05-1998	AT 201662 T AU 733425 B2 AU 2434197 A BR 9708768 A CN 1218443 A ,B DE 69705039 D1 DE 69705039 T2 EP 0892762 A1 ES 2157070 T3 HK 1015757 A1 JP 2000508289 T KR 2000005432 A RU 2165390 C2 TW 399030 B WO 9737934 A1 US 6159636 A	15-06-2001 17-05-2001 29-10-1997 03-08-1999 02-06-1999 05-07-2001 15-11-2001 27-01-1999 01-08-2001 18-01-2002 04-07-2000 25-01-2000 20-04-2001 21-07-2000 16-10-1997 12-12-2000

information on patent family members

PCT/US 02/24684

Form PCT/ISA/210 (patent family annex) (July 1992)