PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{6} : **C01G 45/00, H01M 4/48**	**A1**	**(11) International Publication Number:** **WO 98/46528** **(43) International Publication Date:** 22 October 1998 (22.10.98)

(21) International Application Number: PCT/US98/04940

(22) International Filing Date: 12 March 1998 (12.03.98)

(30) Priority Data:
08/840,872 17 April 1997 (17.04.97) US

(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: DAHN, Jeffrey, R.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). ZHENG, Tao; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: PASTIRIK, Daniel, R. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

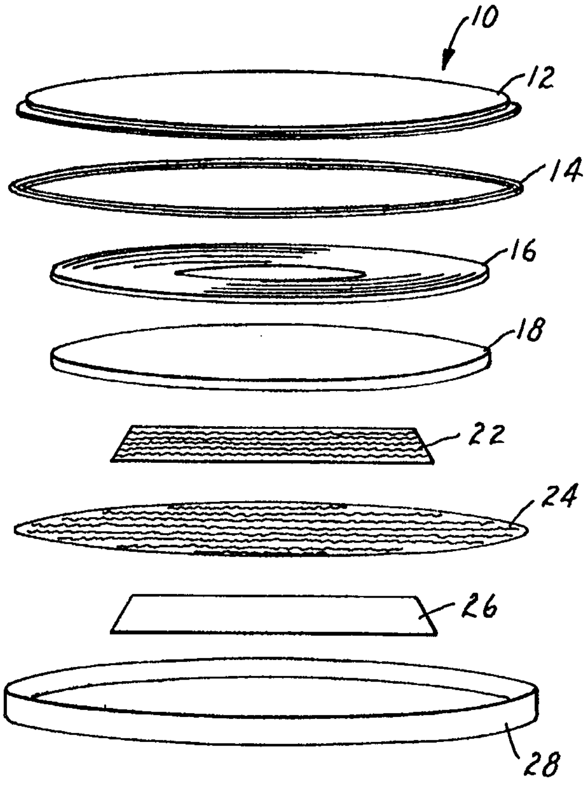
(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW,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

Published
With international search report.

(54) Title: COMPOUNDS USEFUL AS ELECTRODES AND METHOD FOR PREPARING SAME

(57) Abstract

A process for preparing a compound that includes the steps of: (a) preparing a solution comprising (i) a chromium source, (ii) a manganese source, (iii) a lithium source, and (iv) an oxygen source, where the relative amounts of each of the sources are selected to yield, following step (c), a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y \geq 2$, $0.25 < x < 2$, and $z \geq 0$; (b) treating the solution to form a gel; and (c) heating the gel under an inert atmosphere for a time and at a temperature sufficient to yield a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y \geq 2$, $0.25 < x < 2$, and $z \geq 0$. The invention also features a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y > 2$, $0.25 < x < 2$, and $z \geq 0$, and an electrode composition containing this compound.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

COMPOUNDS USEFUL AS ELECTRODES AND METHOD FOR PREPARING SAME

This invention relates to preparing compounds useful as electrode compositions for lithium-ion batteries.

Lithium-ion batteries typically feature a pair of electrodes, at least one of which contains lithium in the form of a lithium-transition metal oxide. These batteries offer the advantages of high energy storage capacity and rechargeability. For optimum performance, it is desirable to maximize electrode capacity between cutoff voltages in the range of about 2.5V to about 4.2V vs. lithium metal.

In a first aspect, the invention features a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y > 2$, $0.25 < x < 2$, and $z \geq 0$. The invention also features an electrode composition that includes this compound. In preferred embodiments, $2 < y < 2.5$ and $0.5 < x \leq 1.5$. In one particularly preferred embodiment, y is about 2.2.

In a second aspect, the invention features a process for preparing a compound that includes the steps of (a) preparing a solution that includes (i) a chromium source, (ii) a manganese source, (iii) a lithium source, and (iv) an oxygen source, the relative amounts of each of the sources being selected to yield, following step (c), a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y \geq 2$, $0.25 < x < 2$, and $z \geq 0$; (b) treating the solution to form a gel; and (c) heating the gel under an inert atmosphere for a time and at a temperature sufficient to yield a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y \geq 2$, $0.25 < x < 2$, and $z \geq 0$.

In preferred embodiments, the gel is heated at a temperature less than about 1000°C, preferably less than about 800°C, and more preferably no greater than about 700°C. The solution preferably is an aqueous solution. The gel is preferably formed by treating the solution with ammonium hydroxide.

The chromium, manganese, lithium, and oxygen sources may be in the form of four separate materials, or in the form of a material that combines two or more of these elements. For example, the chromium source preferably is a compound consisting essentially of chromium and at least one additional element selected from the group consisting of oxygen, nitrogen, carbon, and hydrogen. An example of such a chromium source is a chromium salt such as chromium nitrate. This material acts as a source of both chromium and oxygen. Similarly, the manganese source preferably is a compound consisting essentially of manganese and at least one additional element selected from the group consisting of oxygen, nitrogen, carbon, and hydrogen. An example is a manganese salt such as manganese acetate. Similar to the case of chromium nitrate, this material acts as a source of both manganese and oxygen. The lithium source preferably is a compound consisting essentially of lithium and at least one additional element selected from the group consisting of oxygen, nitrogen, carbon, and hydrogen. An example is a lithium salt such as lithium hydroxide, a material which acts as a source of both lithium and oxygen.

According to one embodiment, the chromium, manganese, lithium, and oxygen sources are selected to yield, following step (c), a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y > 2$, $0.25 < x < 2$, and $z \geq 0$. In another embodiment, the chromium, manganese, lithium, and oxygen sources are selected to yield, following step (c), a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y > 2$, $0.5 < x \leq 1.5$, and $z \geq 0$. In a third embodiment, the chromium, manganese, lithium, and oxygen sources are selected to yield, following step (c), a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y = 2$, $0.25 < x < 2$, and $z \geq 0$. In a fourth embodiment, the chromium, manganese, lithium, and oxygen sources are selected to yield, following step (c), a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y = 2$, $1.0 \leq x \leq 1.5$, and $z \geq 0$.

In a third aspect, the invention features a lithium ion battery that includes: (a)a first electrode that includes a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y \geq 2$, $0.25 < x < 2$, and $z \geq 0$; (b) a second electrode; and (c) an electrolyte, in which the first electrode has a reversible specific capacity of at least 100 mAh/g in the range 2.5V - 4.2V vs. Li metal when discharged at a rate corresponding to full discharge in 10 hours or less.

The invention provides compounds useful as electrode compositions (e.g., cathode compositions) for lithium-ion batteries. The electrode compositions exhibit good performance, as measured, e.g., by reversible specific capacity in the range 2.5V - 4.2V vs. lithium metal. Lithium-ion batteries incorporating such electrode compositions may be repeatedly cycled without substantial loss of performance. The compounds are prepared using a sol-gel process that proceeds under relatively mild conditions (e.g., at temperatures preferably less than about 1000°C) and requires relatively short reaction times (e.g., on the order of 10-24 hours).

Compounds in which y is greater than 2 offer the advantage of minimizing the presence of transition metals (i.e., chromium and manganese) in the lithium layers of the layered oxide. Such transition metals can prevent the free diffusion of intercalated lithium, leading to materials having poor intercalation kinetics and poor performance in lithium batteries.

Other features and advantages of the invention will be apparent from the following description of the preferred embodiments thereof, and from the claims.

Fig. 1 is a series of x-ray diffraction profiles for the materials prepared according to Examples 1-7.

Fig. 2 is a series of expanded views of the x-ray diffraction profiles in the range from 33 to 40 degrees for the materials prepared according to Examples 1, 3, 5, and 7.

Fig. 3 is an exploded perspective view of an electrochemical cell used to test various electrode compositions.

Lithium-chromium-manganese oxides described herein have the general formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y \geq 2$, $0.25 < x < 2$, and $z \geq 0$. These oxides are particularly useful as electrode compositions for lithium-ion batteries. They are preferably prepared in a sol-gel process in which chromium, lithium, manganese, and oxygen sources are combined to form a solution (preferably an aqueous solution), which is then converted to a gel by the addition of a reagent such as ammonium hydroxide (NH_4OH). The gel is then heated under an inert atmosphere (e.g., an argon atmosphere) to convert the gel to the desired oxide.

A variety of materials may be used as the chromium, lithium, manganese, and oxygen sources as long as they are soluble in the medium used to prepare the gel. For example, in the case of aqueous solutions, the chromium, lithium, manganes, and oxygen sources must be water-soluble. A single material may serve as a source for more than one of these elements.

Preferred materials are those in which the elemental constituents (with the exception of chromium, lithium, manganese, and at least some of the oxygen) form volatile by-products during the heating step such that these elemental constituents do not become part of the final oxide product. The resulting oxide product, therefore, contains only lithium, chromium, manganese, and oxygen as its elemental constituents. In this way, the oxide product is essentially free of impurities which might otherwise compromise electrode performance.

Examples of suitable materials include nitrogen-containing compounds (which can liberate nitrogen-containing gas during heating), carbon-containing compounds (which can liberate, e.g., carbon dioxide and/or carbon monoxide during heating), and hydrogen-containing compounds (which can liberate, e.g., water vapor during heating). Specific examples include nitrates, hydroxides, and esters of organic acids such as acetates, citrates, tartrates, and oxalates.

The heating temperature and stoichiometric ratios of reactants determine the crystal structure (and associated parameters such as lattice constants and unit cell volume) of the oxide product, as well as whether the product is a single or multi-phase material. In general, temperatures less than 1000°C are preferred, with temperatures in the range 500-700°C being particularly preferred.

The invention will now be described further by way of the following examples.

EXAMPLES

ELECTROCHEMICAL CELL PREPARATION

Electrodes were prepared as follows. About 12 wt.% $Li_yCr_xMn_{2-x}O_{4+z}$ (prepared as described below), 6 wt.% Kynar Flex 2801 (a vinylidene fluoride-hexafluoropropylene copolymer commercially available from Atochem), 10 wt. % EC/PC (ethylene carbonate/propylene carbonate, 50/50 by volume), 1.5 wt. % Super S carbon black (commercially available from MMM Carbon, Belgium), and 70.5 wt.% acetone were thoroughly mixed by stirring in a sealed bottle at 50°C for four hours to form a slurry. The slurry was then spread in a thin layer (about 150 micrometers thick) on a glass plate using a doctor blade spreader. After evaporating the acetone, the resulting film was peeled from the glass and a circular electrode measuring 1 cm in diameter was punched from the film using an electrode punch. The circular electrode was then weighed and the active mass (the total weight of the circular electrode multiplied by the fraction of the electrode weight made up by $Li_yCr_xMn_{2-x}O_{4+z}$) calculated, after which the circular electrode was sealed in a polyethylene bag with heat sealer until used to assemble an electrochemical cell.

To assemble an electrochemical cell, each circular electrode was first placed in diethyl ether for about 5 minutes to remove EC/PC and form pores in the electrode that the electrolyte will fill during cell construction. The electrodes were then taken into an argon-filled glove box where the electrochemical cell was constructed.

An exploded perspective view of the electrochemical cell is shown in Fig. 3. The anode was a lithium foil having a thickness of 125 micrometers; the anode also functioned as a reference electrode. The cell featured 2320 coin-cell hardware, equipped with a spacer plate (304 stainless steel) and a disc spring (mild steel). The disc spring was selected so that a pressure of about 15 bar would be applied to each of the cell electrodes when the cell was crimped closed. The separator was a Celgard #2502 microporous polypropylene film (Hoechst-Celanese) which had been wetted with a 1M solution of $LiPF_6$ dissolved in a 30:70 volume mixture of ethylene carbonate and diethyl carbonate (Mitsubishi Chemical).

SYNTHESIS

Example 1

50.524g (0.125 moles) of $Cr(NO_3)_3 \cdot 9H_2O$ (Aldrich Chemical Co., 99%) and 18.38g (0.075 moles) of $Mn(CH_3COO)_2 \cdot 4H_2O$ (Aldrich Chemical Co.) were dissolved in 80 mls of distilled water to form a transition metal solution. In a separate beaker, 8.564g (0.2 moles) of $LiOH \cdot H_2O$ (FMC Corp., 98%) was dissolved in 70 mls of distilled water. While stirring, the LiOH solution was added dropwise to the transition metal solution over a period of about 5 minutes. The solution was stirred for about 15 minutes. Finally, about 10 mls of NH_4OH was added dropwise over about 5 minutes to form a gel. The gel was then placed in a "Fisher-Brand" muffle oven set to 170°C to dry and solidify the gel overnight in air. After initial drying, the solidified gel was powdered in a Retsch model Rm-O automatic grinder for about 10 minutes.

The powdered gel was then heated to 500°C using a Lindberg tube furnace equipped with stainless steel furnace tubes and sealed end caps. After the gel had been loaded into the furnace tube, but before initiating heating, the end caps were sealed, and the furnace tube thoroughly purged with UHP-grade argon (Canadian Liquid Air), to remove unwanted air.

UHP-grade argon was passed at a rate of about 150 cc/min through fittings in the sealed end caps during the synthesis. The heating profile was as follows: from 30°C to 150°C in 20 minutes, followed by a 3 hour soak at 150°C. The sample was then heated to 500°C in 40 minutes, soaked for 10 hours, and cooled to room temperature in about one hour to yield a compound having the formula $Li_2Cr_{1.25}Mn_2O_{4+z}$ where $z \geq 0$.

A powder x-ray diffraction pattern for the product was collected using a Siemens D5000 diffractometer equipped with a copper target X-ray tube and a diffracted beam monochromator. Data was collected between scattering angles of 10 degrees and 130 degrees. A portion of the x-ray diffraction profile is shown in Fig. 1. An expanded view of the profile in the range from 33 to 40 degrees is shown in Fig. 2.

The crystal structure was determined based upon the x-ray diffraction data as described in (a) C.J. Howard and R.J. Hill, Australian Atomic Energy Commission Report No. M112 (1986); and (b) D.B. Wiles and R.A. Young, J. Appl. Cryst., 14:149-151 (1981). The diffraction pattern of the sample can be fit by either of two "homeomorphic" crystal structures. These are the layered $LiCoO_2$-like structure with $c/a = (24)^{1/2}$ which gives Bragg peaks in the same positions and with the same powder intensities as the cubic spinel-related structure (space group Fd3m) with cations in 16c (Li) and 16d (Mn,Cr) positions. This structure will be designated "cub/hex."

Lattice constants were determined using least squares refinements to the positions of calculated and measured Bragg peak positions, and were used to calculate unit volume according to the procedure described in standard x-ray diffraction texts, e.g., B.D. Warren, <u>X-Ray Diffraction</u>, Addison-Wesley, Reading, MA (1969). The unit volume refers to the volume of the crystal per formula unit of the material, the formula unit being $Li_yCr_xMn_{2-x}O_{4+z}$. For the cub/hex structure indexed on the cubic spinel-related unit cell, the unit cell contains 9 formula units. For the cub/hex structure indexed on the hexagonal unit cell, the unit cell contains 3/2 formula units. For the hex structure, indexed on the hexagonal unit cell, the unit cell contains 3/2 formula units. For the d-hex structure, the unit cell contains 1 formula unit.

The lattice constants and unit volume for the sample are set forth in Table 1. A comparison of the measured and calculated Bragg peak positions is set forth in Table 2. The calculated values were obtained assuming a layered structure with space group R-3M. The lattice constants used were a = 2.895A and c = 14.190A.

Examples 2-7

Examples 2-7 were prepared following the procedure in Example 1 except that a 2 gram sample of the powdered material was further subjected to a heat treatment in the furnace for 24 hours at the following temperatures: 600°C (Example 2), 700°C (Example 3), 800°C (Example 4), 900°C (Example 5), 1000°C (Example 6), and 1100°C (Example 7). In the case of samples prepared above 700°C, quartz furnace tubes were used. Powder x-ray diffraction patterns were obtained for each sample and are shown in Figures 1 and 2.

The crystal structure, lattice constants, and unit volume were determined for each sample (with the exception of Examples 4 and 6) according to the procedure in Example 1. The results are summarized in Table 1.

The material prepared in Example 2 had a cub/hex structure.

The material prepared in Example 3 exhibited the "layered $LiCoO_2$" structure, which will be designated "hex" here. The measured and calculated Bragg peak positions for Example 3 are shown in Table 3. The calculated values were obtained assuming a layered structure with space group R-3M. The lattice constants used were a = 2.903A and c = 14.426A.

The crystal structure of the material prepared in Example 5 was a layered one, but with a small distortion, analogous to that recently found for layered $LiMnO_2$ by Armstrong and Bruce, Nature 381:499 (1996). The observed and calculated Bragg peak positions for Example 5 are summarized in Table 4. This structure will be designated "d-hex", short for "distorted hexagonal." The calculated values were obtained assuming a layered structure with space group C 2/M. The lattice constants used were a = 5.118A, b = 2.880A, c = 5.161A and beta = 110.94°.

The crystal structure of the material prepared in Example 7 was also a layered or "hex" structure, but with substantially different Bragg peak positions compared to Example 3. The observed and calculated Bragg peak positions for Example 7 are summarized in Table 5. The calculated values were obtained assuming a layered structure with space group R-3M. The lattice constants used were a = 2.9259A and c = 14.537A.

The material prepared in Example 4 was a two phase mixture of the materials of Examples 3 and 5. The material prepared in Example 6 was a two phase mixture of the materials of Examples 5 and 7.

Several electrochemical cells were constructed according to the procedure described above using, as the cathode, samples prepared according to Example 3. Specifically, four cells were prepared using the material of Example 3 and cycled between voltage limits of 2.5V and 4.2V using currents of (a) 1.5 mA/g ("3-1"), (b) 3.75 mA/g ("3-2"), and (c) 15mA/g (two cells) ("3-3" and "3-4"). The first charge capacity, first discharge capacity, and time taken to deliver 148 mAh/g were determined and the results reported in Table 6. The data demonstrates that the capacity is maintained as the current is increased.

Example 8

Example 8 was prepared following the procedure set forth in Example 1 except that the relative amounts of reactants ($Cr(NO_3)_3 \cdot 9H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, and $LiOH \cdot H_2O$)

were selected to yield a product having the formula $Li_2Cr_{1.0}Mn_{1.0}O_{4+z}$ where $z \geq 0$. The crystal structure, lattice constants, and unit cell volume were determined as described in Example 1 and are reported in Table 1.

Examples 9-14

Examples 9-14 were prepared following the procedure in Example 8 except that a 2 gram sample of the powdered material was further subjected to a heat treatment in the furnace for 24 hours at the following temperatures: 600°C (Example 9), 700°C (Example 10), 800°C (Example 11), 900°C (Example 12), 1000°C (Example 13), and 1100°C (Example 14). In the case of samples prepared above 700°C, quartz furnace tubes were used. The crystal structure, lattice constants, and unit cell volume for each sample (with the exception of Examples 9 and 11) were determined as described in Example 8 and are reported in Table 1.

An electrochemical cell was constructed as described above using the material of Example 10, and cycled between voltage limits of 2.5V and 4.2V using a current of 15mA/g. The first charge capacity, first discharge capacity, and time taken to deliver 148 mAh/g were determined and the results reported in Table 6.

Example 15

Example 15 was prepared following the procedure set forth in Example 1 except that the relative amounts of reactants ($Cr(NO_3)_3 \cdot 9H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, and $LiOH \cdot H_2O$) were selected to yield a product having the formula $Li_2Cr_{1.5}Mn_{0.5}O_{4+z}$ where $z \geq 0$. The crystal structure was determined as described in Example 1 and is reported in Table 1.

Examples 16-21

Examples 16-21 were prepared following the procedure in Example 15 except that a 2 gram sample of the powdered material was further subjected to a heat treatment in the furnace for 24 hours at the following temperatures: 600°C (Example 16), 700°C (Example 17), 800°C (Example 18), 900°C (Example 19), 1000°C (Example 20), and 1100°C (Example 21). In the case of samples prepared above 700°C, quartz furnace tubes were used. The crystal structure, lattice constants, and unit cell volume for each sample (with the exception of Example 18) were determined as described in Example 1 and are reported in Table 1.

An electrochemical cell was constructed as described above using the material of Example 17, and cycled between voltage limits of 2.5V and 4.2V using a current of 15mA/g. The first charge capacity, first discharge capacity, and time taken to deliver 148 mAh/g were determined and the results reported in Table 6.

Example 22

Example 22 was prepared following the procedure set forth in Example 1 except that the relative amounts of reactants ($Cr(NO_3)_3 \cdot 9H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, and $LiOH \cdot H_2O$) were selected to yield a product having the formula $Li_{2.2}Cr_{1.25}Mn_{0.75}O_{4+z}$ where $z \geq 0$. The crystal structure, lattice constants, and unit cell volume were determined as described in Example 1 and is reported in Table 1.

Example 23

Example 23 was prepared following the procedure set forth in Example 22 except that a 2 gram sample of the powdered material was further subjected to a heat treatment in the furnace for 24 hours at 700°C. The crystal structure, lattice constants, and unit cell volume for the sample were determined as described in Example 1 and are reported in Table 1.

An electrochemical cell was constructed as described above using the material of Example 23, and cycled between voltage limits of 2.5V and 4.2V using a current of 15mA/g. The first charge capacity, first discharge capacity, and time taken to deliver 148 mAh/g were determined and the results reported in Table 6.

Example 24

Example 24 was prepared following the procedure set forth in Example 1 except that the relative amounts of reactants ($Cr(NO_3)_3 \cdot 9H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, and $LiOH \cdot H_2O$) were selected to yield a product having the formula $Li_2Cr_{0.5}Mn_{1.5}O_{4+z}$ where $z \geq 0$, and the firing temperature was 300°C. The crystal structure, lattice constants, and unit cell volume were not determined.

Examples 25-30

Examples 25-30 were prepared following the procedure in Example 24 except that a 2 gram sample of the powdered material was further subjected to a heat treatment in the furnace for 24 hours at the following temperatures: 600°C (Example 25), 700°C (Example 26), 800°C (Example 27), 900°C (Example 28), 1000°C (Example 29), and 1100°C (Example 30). In the case of samples prepared above 700°C, quartz furnace tubes were used. The crystal structure, lattice constants, and unit cell volume were not determined.

Example 31

Example 31 was prepared following the procedure set forth in Example 1 except that the relative amounts of reactants ($Cr(NO_3)_3 \cdot 9H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, and $LiOH \cdot H_2O$) were selected to yield a product having the formula $Li_2Cr_{0.75}Mn_{1.25}O_{4+z}$ where $z \geq 0$. The crystal structure, lattice constants, and unit cell volume for the sample were determined as described in Example 1 and are reported in Table 1.

Examples 32-37

Examples 32-37 were prepared following the procedure in Example 32 except that a 2 gram sample of the powdered material was further subjected to a heat treatment in the furnace for 24 hours at the following temperatures: 600°C (Example 32), 700°C (Example 33), 800°C (Example 34), 900°C (Example 35), 1000°C (Example 36), and 1100°C (Example 37). In the case of samples prepared above 700°C, quartz furnace tubes were used. The crystal structure, lattice constants, and unit cell volume of Example 36 were determined as described in Example 31 and are reported in Table 1. The crystal structure, lattice constants, and unit cell volume for the remaining examples were not determined.

TABLE 1

Sample	Cr Concentration	Heating conditions	Structure type	a(Å)	b(Å)	c(Å)	volume of unit cell (Å^3)
1	1.25	500C,Ar, 10hrs	cub/hex	2.895		14.190	68.62
2	1.25	600C,Ar, 24hrs	cub/hex	2.894		14.220	68.78
3	1.25	700C,Ar, 24hrs	hex	2.903		14.426	70.18
4	1.25	800C,Ar, 24hrs					
5	1.25	900C,Ar, 24hrs	d-hex	5.118	2.880	5.161	71.07
6	1.25	1000C,Ar, 24hrs					
7	1.25	1100C,Ar, 24hrs	hex	2.926		14.537	71.84
8	1.0	500C,Ar, 10hrs	cub/hex	2.894		14.198	68.63
9	1.0	600C,Ar, 10hrs					
10	1.0	700C,Ar, 24hrs	hex	2.901		14.357	69.78
11	1.0	800C,Ar, 24hrs					
12	1.0	900C,Ar, 24hrs	d-hex	5.175	2.855	5.201	71.239
13	1.0	1000C,Ar, 24hrs	d-hex	5.183	2.863	5.210	71.663
14	1.0	1100C,Ar, 24hrs	d-hex	5.195	2.862	5.223	71.901
15	1.5	500C,Ar, 20hrs	cub/hex				
16	1.5	600C,Ar, 24hrs	hex	2.900		14.205	68.98
17	1.5	700C,Ar, 24hrs	hex	2.899		14.431	70.03
18	1.5	800C,Ar, 24hrs					
19	1.5	900C,Ar, 24hrs	hex	2.910		14.456	70.66
20	1.5	1000C,Ar, 24hrs	hex	2.908		14.447	70.55
21	1.5	1100C,Ar, 24hrs	hex	2.915		14.458	70.92
22	Li(2.2)Cr (1.25)	500C,Ar, 10hrs	Cub/hex	2.823		14.185	68.532

23	Li(2.2)Cr (1.25)	700C Ar, 24hrs	hex	2.8967		14.41	69.81
24	0.5	300C,air, 10hrs					
25	0.5	600C,Ar, 24hrs					
26	0.5	700C,Ar, 24hrs					
27	0.5	800C,Ar, 24hrs					
28	0.5	900C,Ar, 24hrs					
29	0.5	1000C,Ar, 24hrs					
30	0.5	1100C,Ar, 24hrs					
31	0.75	500C,Ar, 10hrs	cub/hex	2.892		14.173	68.45
32	0.75	600C,Ar, 24hrs					
33	0.75	700C,Ar, 24hrs					
34	0.75	800C,Ar, 24hrs					
35	0.75	900C,Ar, 24hrs					
36	0.75	1000C,Ar, 24hrs	hex	5.230	2.846	5.243	71.86
37	0.75	1100C,Ar 24hrs					

TABLE 2

Miller Indices (hkl)	Observed Angle (deg.)	Calculated Angle (deg.)
0,0,3	18.67	18.759
1,0,-1	36.49	36.395
0,0,6	38.10	38.046
1,0,2	38.10	38.072
1,0,-4	44.26	44.241
1,0,5	48.34	48.449
1,0,-7	58.54	58.558
1,0,8	64.39	64.335
1,1,0	64.39	64.371
1,1,3	67.65	67.702

TABLE 3

Miller Indices (hkl)	Oberserved Angle (deg.)	Calculated Angle (deg.)
0,0,3	18.46	18.449
1,0,-1	36.27	36.273
0,0,6	37.38	37.399
1,0,2	37.89	37.901
1,0,-4	43.93	43.900
1,0,5	47.99	47.998
1,0,-7	57.90	57.852
1,0,8	63.45	63.484
1,1,0	64.14	64.167
1,1,3	67.40	67.396
2,0,1	76.02	75.998

TABLE 4

Miller Indices (hkl)	Observed Angle (deg.)	Calculated Angle (deg.)
0,0,1	18.43	18.403
2,0.-1	35.49	35.459
1,1,0	36.43	36.416
0,0,2	37.32	37.304
1,1,-1	37.70	37.773
2,0,-2	42.68	42.709
1,1,1	44.23	44.215
1,1,-2	47.72	47.634
2,0,-3	56.42	56.440
0,0,3	57.33	57.336
1,1,2	58.20	58.234

TABLE 5

Miller Indices (hkl)	Observed Angle (deg.)	Calculated Angle (deg.)
0,0,3	18.30	18.308
1,0,-1	35.99	35.976
0,0,6	37.11	37.106
1,0,2	37.57	37.591
1,0,-4	43.55	43.540
1,0,5	47.61	47.602
1,0,-7	57.36	57.364
1,0,8	62.95	62.949
1,1,0	63.62	63.599
1,1,3	66.79	66.794

TABLE 6

Material	Example	Heating Temp. (°C)	Unit cell volume (Å^3)	First Charge capacity (mAh/g)	Upper cutoff voltage (V)	First discharge capacity (mAh/g)	Time taken to deliver 148 mAh/g (hours)
$Li_2Cr_{1.25}Mn_{0.75}O_4$	3-1	700°C	70.22	178	4.2	150	100
$Li_2Cr_{1.25}Mn_{0.75}O_4$	3-2	700°C	70.22	166	4.2	137	40
$Li_2Cr_{1.25}Mn_{0.75}O_4$	3-3	700°C	70.22	138	4.2	106	10
$Li_2Cr_{1.25}Mn_{0.75}O_4$	3-4	700°C	70.22	206	4.5*	137	10
$Li_{2.2}Cr_{1.25}Mn_{0.75}O_4$	23	700°C	69.81	175	4.2	117	10
$Li_2Cr_{1.5}Mn_{0.5}O_4$	17	700°C	70.03	159	4.2	110	10
$Li_2Cr_{1.0}Mn_{1.0}O_4$	10	700°C	69.78	170	4.2	110	10

*Same capacity expected at 4.2V upper cutoff due to shape of voltage profile.

Other embodiments are within the following claims.

What is claimed is:

1. A compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y > 2$, $0.25 < x < 2$, and $z \geq 0$.

2. An electrode composition comprising the compound of claim 1.

3. A process for preparing the compound of claim 1 comprising the steps of:

(a) preparing a solution comprising (i) a chromium source, (ii) a manganese source, (iii) a lithium source, and (iv) an oxygen source,

the relative amounts of each of said sources being selected to yield, following step (c), a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y \geq 2$, $0.25 < x < 2$, and $z \geq 0$;

(b) treating said solution to form a gel; and

(c) heating said gel under an inert atmosphere for a time and at a temperature sufficient to yield a compound having the formula $Li_yCr_xMn_{2-x}O_{4+z}$ where $y \geq 2$, $0.25 < x < 2$, and $z \geq 0$.

4. A process according to claim 3 comprising heating said gel at a temperature less than about 1000°C.

5. A process according to claim 3 wherein said solution comprises an aqueous solution.

6. A process according to claim 3 comprising treating said solution with ammonium hydroxide to form said gel.

7. A process according to claim 3 wherein said chromium source comprises a compound consisting of

chromium and at least one additional element selected from the group consisting of oxygen, nitrogen, carbon, and hydrogen.

8. A process according to claim 7 wherein said chromium source comprises chromium nitrate.

9. A process according to claim 3 wherein said manganese source comprises a compound consisting of manganese and at least one additional element selected from the group consisting of oxygen, nitrogen, carbon, and hydrogen.

10. A process according to claim 9 wherein said manganese source comprises manganese acetate.

11. A process according to claim 3 wherein said lithium source comprises a a compound consisting essentially of lithium and at least one additional element selected from the group consisting of oxygen, nitrogen, carbon, and hydrogen.

12. A process according to claim 11 wherein said lithium source comprises lithium hydroxide.

13. A lithium ion battery comprising:

(a) a first electrode comprising the compound of claim 1;

(b) a second electrode; and

(c) an electrolyte,

said first electrode having a reversible specific capacity of at least 100 mAh/g in the range 2.5V - 4.2V vs. Li metal when discharged at a rate corresponding to full discharge in 10 hours or less.

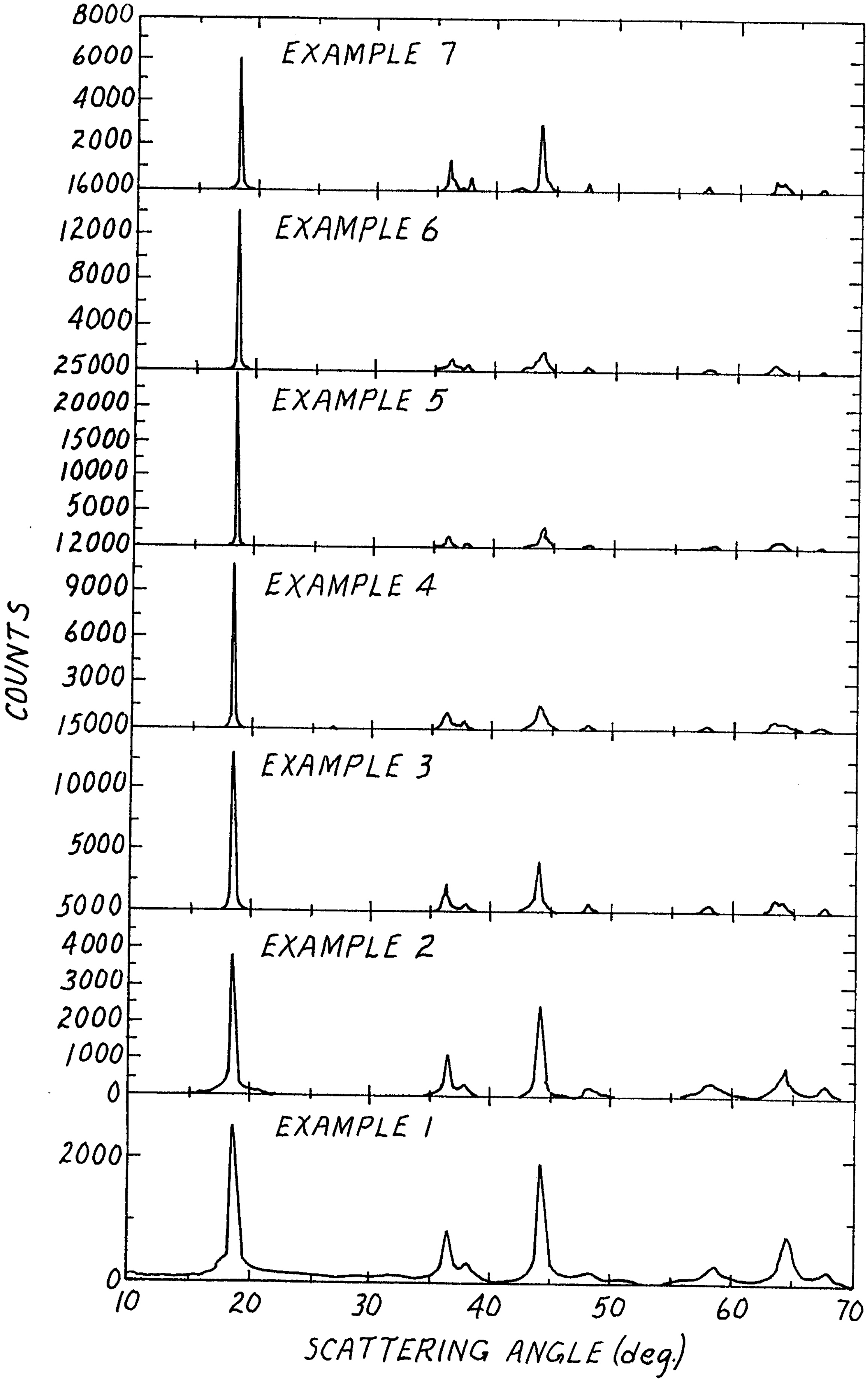

EXAMPLE 7
8000
6000
4000
2000
16000
EXAMPLE 6
12000
8000
4000
25000
EXAMPLE 5
20000
15000
10000
5000
12000
EXAMPLE 4
9000
6000
3000
15000
EXAMPLE 3
10000
5000
5000
EXAMPLE 2
4000
3000
2000
1000
0
EXAMPLE 1
2000
0
COUNTS
10
20
30
40
50
60
70
SCATTERING ANGLE (deg.)

FIG. 1

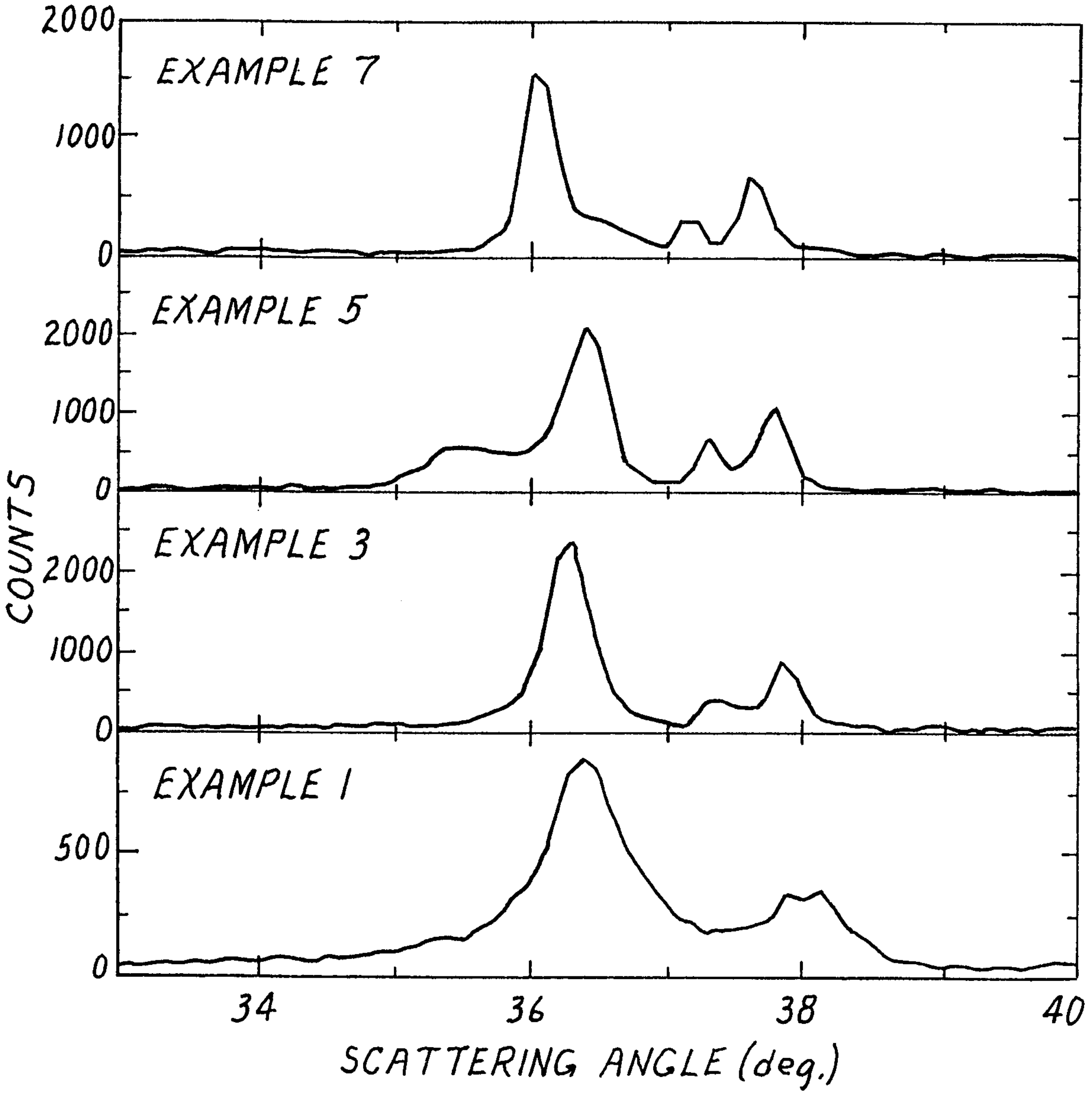

2000
EXAMPLE 7
1000
0
EXAMPLE 5
2000
1000
0
COUNTS
EXAMPLE 3
2000
1000
0
EXAMPLE 1
500
0
34
36
38
40
SCATTERING ANGLE (deg.)

FIG. 2

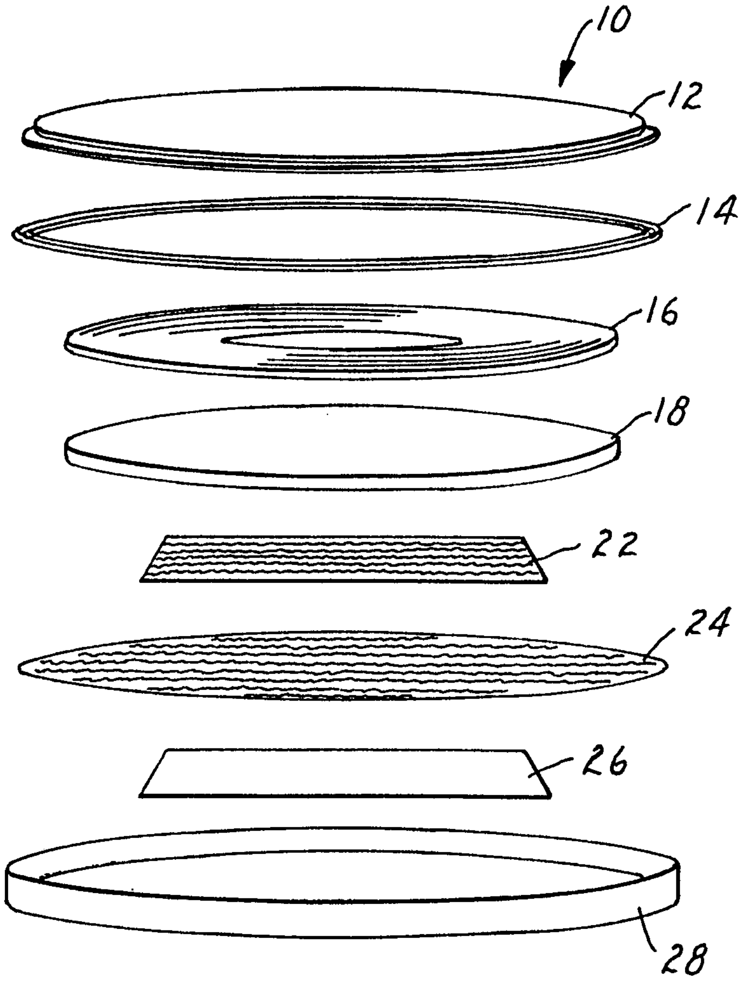


FIG. 3

INTERNATIONAL SEARCH REPORT

Int .ional Application No
PCT/US 98/04940

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01G45/00 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 6 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 124, no. 10, 4 March 1996 Columbus, Ohio, US; abstract no. 122067, AZUMA: XP002067628 see abstract & JP 07 272 765 A (SONY) ---	1
A	FR 2 733 632 A (JAPAN STORAGE BATTERY CO LTD) 31 October 1996 see page 6; claim 1 ---	1-11
A	DAVIDSON I J ET AL: "RECHARGEABLE CATHODES BASED ON LI2CRXMN2-XO4" JOURNAL OF POWER SOURCES, vol. 54, no. 2, 1 April 1995, pages 205-208, XP000542220 --- -/--	1

☒ 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 10 June 1998	Date of mailing of the international search report 30/06/1998
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 LIBBERECHT, E

1

Int ional Application No
PCT/US 98/04940

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 605 773 A (P.C. ELLGEN) 25 February 1997 see column 12 -----	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. .ional Application No
PCT/US 98/04940

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2733632 A	31-10-1996	JP 8298115 A	12-11-1996
		DE 19615800 A	05-12-1996
		US 5738957 A	14-04-1998
		US 5677087 A	14-10-1997
US 5605773 A	25-02-1997	AU 7181596 A	12-06-1997
		EP 0779669 A	18-06-1997
		JP 9194214 A	29-07-1997