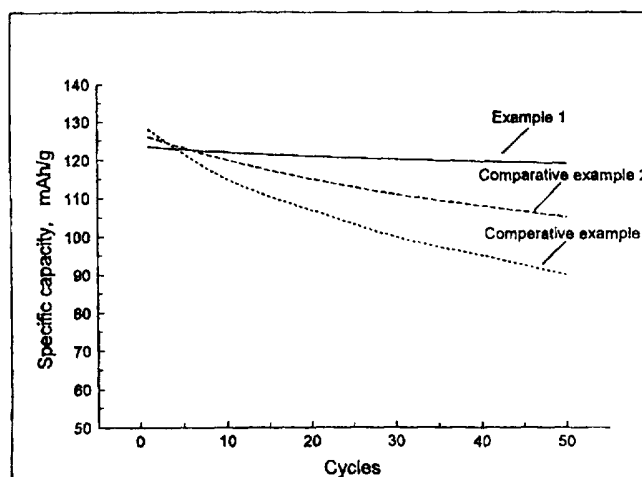




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<p>(21) International Application Number: PCT/US96/19152 (22) International Filing Date: 2 December 1996 (02.12.96) (30) Priority Data: 60/007,997 5 December 1995 (05.12.95) US 08/665,396 18 June 1996 (18.06.96) US (60) Parent Application or Grant (63) Related by Continuation US 08/665,396 (CON) Filed on 18 June 1996 (18.06.96) (71) Applicant (for all designated States except US): FMC CORPORATION [US/US]; 1735 Market Street, Philadelphia, PA 19103 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MANEV, Vesselin [BG/US]; 1852-H Robinwood Road, Gastonia, NC 28054 (US). FAULKNER, Titus [CA/US]; 2524-A Cherbough Way, Gastonia, NC 28054 (US). (74) Agents: LINKER, Raymond, O., Jr. et al.; Bell, Seltzer, Park & Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US).</p>		<p>(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, 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, SK (Utility model), TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), 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).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: HIGHLY HOMOGENEOUS SPINEL $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ INTERCALATION COMPOUNDS AND METHOD FOR PREPARING SAME



(57) Abstract

A novel method of preparing a spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compound with low lattice distortion and a highly ordered and homogeneous structure for 4 V secondary lithium and lithium ion cells is provided. The method of preparing the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compound comprises mixing at least one manganese compound with at least one lithium compound and firing the mixture at three different temperature ranges with corresponding gas flow rates to form the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compounds. The spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compounds have a mean X value of between about 0.01 and 0.05 and a full width at half maximum of the x-ray diffraction peaks at a diffraction angle 2θ of planes (400) and (440) using $\text{CuK}\alpha_1$ rays of between about 0.10° and 0.15° . The spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compounds may be used in the positive electrodes of secondary lithium and lithium ion cells to provide cells having high specific capacities and long cycling lives.

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HIGHLY HOMOGENEOUS SPINEL $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ INTERCALATION
COMPOUNDS AND METHOD FOR PREPARING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is related to commonly owned
co-pending provisional application Serial No. 60/007997
filed December 5, 1995, and claims the benefit of its
5 earlier filing date under 35 U.S.C. § 119(e).

FIELD OF THE INVENTION

This invention relates to spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$
intercalation compounds, and particularly to the use of
spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compounds in 4 V
10 secondary lithium and lithium ion batteries.

BACKGROUND OF THE INVENTION

Heretofore, lithium intercalation compounds
such as LiMn_2O_4 have been used in positive electrodes
for 4 V secondary lithium and lithium ion batteries.
15 The spinel LiMn_2O_4 intercalation compound was first
obtained by Wickham and Croft by heating lithium
carbonate and manganese oxide in 1:2 lithium to
manganese molar ratio. D. G. Wickham and W. J. Croft,
J. Phys. Chem. Solids, 7, 351 (1958). Wickham and
20 Croft also reported that using an excess of lithium in
the reaction mixture led to formation of Li_2MnO_3 , while
an excess of manganese led to a mixture containing
 Mn_2O_3 . These two compounds are intermediate products of
the solid state chemical reactions which take place
25 during the high temperature spinel synthesis of the
spinel LiMn_2O_4 and can be present at any time when the
reactions are not fully completed. W. Howard, *Ext.*
Abstr., 7 IMLB, 281 (Boston, 1994)

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As demonstrated in U.S. Pat. No. 4,426,253 to Hunter, the acid treatment of LiMn_2O_4 forms a $\lambda\text{-MnO}_2$ which can be used in a positive electrode for electrochemical power sources. It was later discovered that the spinel LiMn_2O_4 could be used as the positive electrode for a secondary lithium cell. Thackery et al., *Material Research Bulletin*, 18, 461 (1983). Thackery et al. demonstrated that the potential-composition curves have two reversible plateaus, respectively at 4 and 2.8 V versus a lithium electrode.

The effect of synthesis temperature on the electrochemical performance of the secondary lithium cell using the 2.8 V plateau of spinel LiMn_2O_4 has been described in, e.g., U.S. Pat. No. 4,828,834 to Nagaura et al. Nagaura et al. determined that an optimal synthesis temperature for LiMn_2O_4 using lithium carbonate and manganese dioxide is in the range of between 430-520°C. Using the 2.8 V charge-discharge plateau, Nagaura et al. also determined that LiMn_2O_4 compounds having a full width at half maximum between 1.1° and 2.1° of a peak 2θ equal to 46.1° by x-ray diffraction analysis using $\text{FeK}\alpha$ rays possess favorable cycling performance when used as the active material in cathodes for secondary lithium cells. Furthermore, Nagaura et al. teaches that spinels having a full width at half maximum less than 1.1° do not possess the desired discharging capacity.

Recently, the effect of the higher synthesis temperature on the reversible capacity of the 4 V plateau was described. V. Manev et al., *J. Power Sources*, 43-44, 551 (1993) and U.S. Pat. No. 5,211,933 to Barboux et al. Manev et al. determined that the synthesis of spinel LiMn_2O_4 for secondary lithium cells should be performed at temperatures lower than 750°C. Barboux et al. stated that low temperature processes between 200° and 600°C yield finer size particles of LiMn_2O_4 , do not affect the capacity of the electrolytic

cells, and enhance the cycling behavior of the spinel. The decrease in the capacity associated with the increase in the synthesis temperature at temperatures higher than 800°C was explained by a significant oxygen
5 loss at temperatures higher than 800°C. Manev et al., *J. Power Sources*, 43-44, 551 (1993).

In U.S. Pat. No. 5,425,932 to Tarascon, a different approach for employing synthesis temperatures greater than 800°C was described which involves an
10 additional slow cooling step with a cooling rate slower than 10°C/h in order to form a spinel with increased cell capacity. Even though this method may increase the capacity of the cell, it may be the source of considerable nonhomogeneous oxygen distribution in the
15 final product, because the oxygen content is a function of firing temperature. For example, the oxygen content in the bulk may be lower than stoichiometric, while an oxygen rich spinel may form on the surface of the particles.

20 As described in R. J. Gummow et al. *Solid State Ionics*, 69, 59 (1994)), an infinite number of high lithium content stoichiometric spinel phases exist with a general formula $\text{Li}_{1-x}\text{Mn}_{2-x}\text{O}_4$ where $(0 \leq x \leq 0.33)$. Gummow et al. also states that an infinite series of
25 oxygen rich defect spinel phases exist with a general formula $\text{LiMn}_2\text{O}_{4+y}$ where $(0 \leq y \leq 0.5)$. The possibility that X and Y may have negative values has been described for the ranges $-0.1 \leq x \leq 0$ for $\text{Li}_x\text{Mn}_2\text{O}_4$ in U.S. Pat. No. 5,425,932 to Tarascon and $-0.1 \leq y \leq 0$ for $\text{LiMn}_2\text{O}_{4+y}$ in V.
30 Manev et al., *J. Power Sources*, 43-44, 551 (1993)). As suggested by Gummow et al. and U.S. Pat. No. 5,425,932 to Tarascon et al., the variation of the lithium and oxygen content are accompanied by considerable variation of the spinel lattice parameters.

35 The existence of an infinite number of lithium manganese spinel phases and the existence of intermediate compounds, thermodynamically stable in the

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temperature range of spinel preparation but inactive in the 4 V discharge range, namely Li_2MnO_3 and Mn_2O_3 , demonstrate that the preparation of highly homogenous spinel compounds is extremely complicated. However, a highly homogenous compound is desirable for positive electrodes of secondary lithium cells to provide high specific capacity and a negligible capacity fade as a function of the number of charge-discharge cycles.

SUMMARY OF THE INVENTION

10 The present invention provides a method of preparing a spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compound with low lattice distortion and a highly ordered and homogeneous structure for 4 V secondary lithium and lithium ion cells having high specific capacity and long cycling life.

The method of preparing a spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compound comprises mixing at least one manganese compound with at least one lithium compound and firing the mixture at a temperature of between about 400°C and 500°C for at least about four hours in the presence of a gas with a gas flow rate in the range of between about 0.5 l/gh and 5.0 l/gh to form an oxygen rich spinel. The oxygen rich spinel is fired at a temperature of between 500°C and 600°C for at least about ten hours in the presence of gas flow with a flow rate of between about 0.1 l/gh and 1.0 l/gh to form a distorted stoichiometric $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel. The distorted stoichiometric spinel is then fired at a temperature between 700°C and 800°C for at least about ten hours in the presence of a gas flow with a gas flow rate of between about 0.005 l/gh and 0.2 l/gh to form an ordered stoichiometric $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel. The spinel is subsequently cooled at a rate of at least 20°C an hour at a flow rate of between 0 l/gh and 1.0 l/gh.

35 The spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compound prepared according to the present invention has a mean

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X value of between about 0.01 and 0.05 and a full width at half maximum of the x-ray diffraction peaks at a diffraction angle 2θ of planes (400) and (440) using $\text{CuK}\alpha_1$ rays of between about 0.10° and 0.15° . The mean
5 crystallite size of the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compounds is between about 3,000 to 30,000 angstroms. The highly ordered and homogeneous spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compounds may be used in the positive electrodes of secondary lithium and lithium ion cells
10 to provide cells having high specific capacity and long cycling life.

These and other features and advantages of the present invention will become more readily apparent to those skilled in the art upon consideration of the
15 following detailed description and accompanying drawings which describe both the preferred and alternative embodiments of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an x-ray diffraction profile with
20 $\text{CuK}\alpha_1$ rays in the range of $15 < 2\theta < 80$ for a distorted stoichiometric spinel formed after the second firing step in accordance with the present invention.

FIG. 2 is an x-ray diffraction profile with
25 $\text{CuK}\alpha_1$ rays in the range of $15 < 2\theta < 80$ for an ordered stoichiometric spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_2$ compound formed according to the present invention.

FIG. 3 is a diagram showing temperature and gas flow rate values as a function of synthesis time according to the preferred method of preparing the
30 spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ of the invention.

FIGS. 4A and 4B are x-ray diffraction profiles corresponding to $\text{CuK}\alpha_1$ rays of the (400) and (440) diffraction peaks of the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compound of the present invention.
35

FIG. 5 is a graph illustrating the comparison between the x-ray diffraction profiles, corresponding

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to $\text{CuK}\alpha_1$ rays of the (400) reflection peaks, of the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ material of the present invention and comparative examples, displayed on the second x-axis as a function of lattice a-axis parameter of the unit
5 cell.

FIG. 6 is a graph trace showing the variation of the a-axis of the unit cell parameters versus the lithium/manganese ratio of the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ of the present invention at a cooling rate 100°C/h .

10 FIG. 7 is a graph illustrating the comparison between the x-ray diffraction profiles corresponding to $\text{CuK}\alpha_1$ rays of (400) reflection peaks, of spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ of the present invention and comparative examples, displayed on the second x-axis as a function of the
15 2Li/Mn ratio.

FIG. 8 is a diagram showing the concept of main lattice distortion in spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compounds.

FIG. 9 is a graph illustrating the dependence
20 of discharge specific capacities on the charge-discharge cycle numbers of the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ compound of the present invention and of the comparative examples.

DETAILED DESCRIPTION OF THE INVENTION

25 According to the method of the present invention, a low crystal lattice distortion spinel intercalation compound with a general formula $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ is prepared from a starting mixture which includes at least one manganese compound and at least one lithium
30 compound. The at least one manganese compound is selected from the group consisting of manganese salts and manganese oxides. Exemplary manganese salts and oxides include MnO_2 , Mn_2O_3 , Mn_3O_4 , MnCO_3 , MnSO_4 , $\text{Mn}(\text{NO}_3)_2$, $\text{Mn}(\text{CH}_3\text{CO}_2)_2$, and mixtures thereof. The at least one
35 lithium compound is selected from the group consisting of lithium salts and lithium oxides. Exemplary lithium

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salts and oxides include Li_2O , LiOH , LiNO_3 , Li_2CO_3 ,
 Li_2SO_4 , LiNO_3 , LiCH_3CO_2 , and mixtures thereof. The at
least one manganese compound and at least one lithium
compound are mixed in a lithium to manganese mole ratio
5 of between about 1.02:2 and 1.1:2.

In order to form this spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$
intercalation compound, the mixture is initially fired
at a temperature range of between about 400°C and
 500°C , preferably about 450°C , in the presence of a gas
10 flow with a flow rate between about 0.5 l/gh and 5.0
l/gh. The gas used in the gas flow is preferably air
or a gas mixture having an oxygen content of between
about 5 and 100% oxygen by volume. During this firing
step, a predominantly high oxygen content spinel
15 $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_{4+y}$ is produced. A high gas flow rate is
maintained in order to lead away from the reaction
mixture inert gases and vapors such as H_2O , CO_2 and NO_2
generally generated from the manganese and lithium
compounds and to deliver oxygen to the spinel in order
20 to avoid formation of Mn_3O_4 and LiMnO_2 . The temperature
of the initial firing step is maintained for a soak
time of at least about 4 hours, and preferably for at
least about 10 hours, to form the oxygen rich spinel.
Once the initial firing step is concluded, the oxygen
25 rich spinel material may be allowed to cool prior to
any subsequent firing steps.

The oxygen rich spinel is subsequently fired
at a temperature of between about 500°C and 600°C ,
preferably between about 550°C and 600°C , in the
30 presence of a gas flow of between about 0.1 l/gh and
1.0 l/gh. The gas used is preferably air or a gas
mixture containing oxygen as described above. A
comparatively high gas flow rate is maintained in the
second firing step to avoid the reduction processes
35 which can be caused by inert gas evolution from
unreacted raw materials during the first firing or from
intermediate products. During the second firing, a

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spinel compound nearly stoichiometric with respect to oxygen and with considerably disordered structures is produced. The temperature of the second firing step is maintained for a soak time of at least about 10 hours, 5 and preferably at least about 48 hours. Once the second firing step is concluded, the x-ray diffraction pattern of the intermediate product, i.e., the distorted $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel, is characteristic of a typical spinel with no traces or reflections 10 corresponding to other phases, but with broad peaks. After the second firing step is finished, the distorted spinel may be allowed to cool prior to subsequent firing steps.

The distorted $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel is 15 subsequently subjected to a third firing step at a temperature of between about 700°C and 800°C, preferably between about 700°C and 750°C, and in the presence of a gas flow at a flow rate of between about 0.005 l/gh and 0.2 l/gh. The gas used in the gas flow 20 is preferably air or a gas mixture containing oxygen as described above. During the third firing step, the temperature range and gas flow rate is sufficiently high to deliver oxygen for oxidation of the intermediate products, e.g., Mn_2O_3 and LiMnO_2 , formed in 25 the prior firing steps and present although possibly undetected by x-ray diffraction analysis. Nevertheless, the temperature range and gas flow rate are low enough to prevent loss of a considerable amount of lithium from the reaction mixture and to prevent the 30 formation of a lithium concentration gradient between the surface and the bulk of the spinel particles. Once the third firing step is completed, an ordered stoichiometric $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel is produced. The temperature of the third firing step is maintained for 35 a soak time of preferably at least about 10 hours, and preferably at least about 24 hours.

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At the conclusion of the third firing step, the mixture is allowed to cool at a rate of greater than about 20°C per hour and preferably greater than about 50°C per hour with a gas flow rate of between
5 about 0 and 1.0 l/gh. As described above with respect to the firing steps, the gas flow used during cooling can be air or a gas mixture containing oxygen.

Alternatively, the firing steps of the method described above may include changes in the temperature
10 and the gas flow rate within the described ranges. In other words, the temperature and/or gas flow rate may be increased or decreased within their respective ranges during the firing steps. Additionally, the gas delivered to the spinel during the firing steps may
15 also vary in oxygen content and gases used during the firing steps may be changed. Although the firing temperatures are preferably maintained for the soak times described above, longer soak times tend to provide an improved spinel compound. Nevertheless, the
20 soak times are typically dictated by commercial feasibility and extremely long soak times may not be desired. As described above, the spinel material may be allowed to cool between firing steps; but for reasons of efficiency, the firing steps are preferably
25 performed consecutively without cooling of the spinel material.

The spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compounds prepared according to the present invention possess improved properties over conventional $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$
30 spinels. The spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ of the invention is a highly ordered and homogeneous structure having a high specific capacity. The improved physicochemical and electrochemical properties of the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinels of the invention are independent of the nature of the
35 manganese compounds and lithium compounds used to form the spinel. The $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinels prepared according to the present invention have a mean X value of between

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about 0.01 and 0.05. The relatively small range of mean X values provides a spinel which exhibits a high initial capacity. In addition, the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinels of the present invention exhibit a full width at half maximum of the x-ray diffraction peaks at a diffraction angle 2θ of planes (400) and (440) using $\text{CuK}\alpha_1$ rays of between about 0.10° and 0.15° . Spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compounds having lower widths at half maximum have correspondingly lower random lattice distortion and narrower distribution of lithium/manganese ratios. When spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compounds having widths at half maximum in this range are used in the positive electrode of rechargeable lithium cells, the decrease in the specific capacity during cycling is negligible and thus the lithium cells exhibit long cycling lives. The mean crystallite size of the spinels of the invention is between about 3,000 and 30,000 angstroms.

The spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ compounds may be used in positive electrodes in electrochemical cells. The $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel material is typically combined with a conductive agent such as graphite or carbon black and a binder material such as polyvinylidene difluoride (PVDF) and dispersed in a solvent such as n-methyl pyrrolidinone (NMP) (e.g. 1-methyl-2-pyrrolidinone) to form a slurry. The slurry is typically spread on aluminum and then heated to evaporate the solvent to form a dry electrode material. The dry electrode is then compressed by rolling, pressing, or other known methods, and cut into, for example, a disk, to form the positive electrode. The electrode is then placed inside an electrochemical cell with a lithium counterelectrode and an electrolyte such as EC:DMC/ LiPF_6 .

The present invention will be further illustrated by the following nonlimiting examples.

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As used in these examples, the term "crystallite size" is defined with the presumption that all the crystallites are equivalent and have a cubic shape, using the following formula:

$$L = 6/\rho A$$

wherein L is the crystallite length size, ρ is spinel density and A is the specific surface area measured by the BET method. Single point BET measurements were determined using a Quantachrome Monosorb BET instrument.

The planar spacing based on the (400) reflection peaks is calculated using the Bragg equation:

$$d = \lambda / 2 \sin \theta$$

wherein $\lambda = 1.54056\text{\AA}$ and is the wavelength of $\text{CuK}\alpha_1$ radiation.

The lattice parameter a, corresponding to the plane (400) is calculated using the following formula:

$$a^2 = (i^2 + j^2 + k^2) d^2$$

where i, j, and k are the Miller indexes.

EXAMPLE 1

A spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ compound with mean X value of about 0.025 was prepared by heating together an intimate mixture of LiOH and MnCO_3 in a lithium/manganese mole ratio of 1.05:2. Initially, the mixture was fired for 24 h at about 450°C with an air flow rate of 4 l/gh. Then, the reaction mixture was fired for 48 h at about 550°C, while the air flow rate was decreased and maintained at approximately 0.5 l/g.h. FIG. 1 illustrates the x-ray diffraction profile corresponding to $\text{CuK}\alpha_1$ rays in the range $15 < 2\theta < 80$ of the intermediate product formed after the second firing at 550°C. FIG. 1 shows that after the second firing, a distorted but extremely pure spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ phase is produced. The mixture was then fired at about 750°C for 72 h, while the air flow rate

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was decreased and maintained at 0.1 l/g.h. The mixture was cooled at the rate 100°C per hour, with zero air flow. The x-ray diffraction profile corresponding to $\text{CuK}\alpha_1$ rays in the range $15 < 2\theta < 80$ of the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ compound formed is illustrated in FIG. 2. FIG. 3 is a diagram showing the temperature and air flow rate as a function of synthesis time for this example.

As illustrated in FIGS 4A and 4B, the full width at half maximum of the x-ray diffraction peaks of planes (400) and (440) referring to $\text{CuK}\alpha_1$ rays for 2θ were 0.124 and 0.146 degrees, respectively. The specific surface area measured by BET was 3.1 m^2/g and the mean crystallite size was about 4600 A.

The prepared spinel $\text{Li}_{1+0.025}\text{Mn}_{2-0.025}\text{O}_4$ compound was mixed with 10 % graphite and 5 % PVDF binder and dispersed in NMP solvent to form a slurry. The slurry was spread on Al foil and then heated to evaporate the NMP solvent. The dry electrode was then pressed at 500 kg/cm^2 and cut into a disk test sample electrode having a diameter of about 1 cm and a thickness of about 0.015 cm. The prepared test electrode was placed inside an electrochemical cell with a lithium counter electrode and with an EC:DMC/ LiPF_6 electrolyte. A charging-discharging test was conducted with a 1 h charge-discharge rate and 3 - 4.5 V voltage limits.

COMPARATIVE EXAMPLE 1

A spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ compound with mean X value of about 0.025 was prepared by heating together an intimate mixture of LiOH and MnCO_3 in the same mole ratio (1.05:2) as Example 1. The mixture was fired once at a temperature of 750°C for 72 h at an air flow rate of 1 l/g.h. The mixture was subsequently cooled at the rate of 100°C per hour with zero air flow as in Example 1.

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The full width at half maximum of the x-ray diffraction peaks of planes (400) and (440) referring to $\text{CuK}\alpha_1$ rays for 2θ were 0.308 and 0.374 degrees, respectively. The specific surface area measured by
5 BET was $2.7 \text{ m}^2/\text{g}$ and the mean crystallite size was about 5300 Å.

The spinel $\text{Li}_{1+0.025}\text{Mn}_{2-0.025}\text{O}_4$ positive test electrode and electrochemical cell were prepared in the same manner as in Example 1. Additionally, the cell
10 charge-discharge characteristics were measured under the same conditions as Example 1.

COMPARATIVE EXAMPLE 2

A spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ compound with mean X value of about 0.025 was prepared by heating together an
15 intimate mixture of LiOH and MnCO_3 in the same Li/Mn mole ratio (1.05:2) as Example 1. The mixture was fired in the same three consecutive temperature ranges and with the same duration as Example 1, but at a constant air flow rate of 1 l/gh. As in Example 1, the
20 mixture was cooled at a rate of 100°C per hour, with zero air flow.

The full width at half maximum of the x-ray diffraction peaks of planes (400) and (440) referring to $\text{CuK}\alpha_1$ rays for 2θ , were 0.216 and 0.262 degrees,
25 respectively. The specific surface area measured by BET was $2.8 \text{ m}^2/\text{g}$ and the mean crystallite size was about 5100 Å.

The spinel $\text{Li}_{1+0.025}\text{Mn}_{2-0.025}\text{O}_4$ positive test electrode and electrochemical cell were prepared in the
30 same manner as in Example 1. Additionally, the cell charge-discharge characteristics were measured under the same conditions as Example 1.

FIG. 5 illustrates the comparison between the x-ray diffraction profiles referring to $\text{CuK}\alpha_1$ rays of
35 (400) reflection peaks of spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ materials of Example 1 and the Comparative Examples 1 and 2. For

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crystal compounds with a crystallite size higher than 3,000 angstroms such as those formed in Example 1 and Comparative Examples 1 and 2, x-ray divergence due to crystallite size does not take place in x-ray
5 diffraction analysis which employs wavelengths of several angstroms. Thus, the different (400) plane profiles observed in FIG. 5 are based on the different degrees of lattice distortion. This is supported by the fact that the mean crystallite sizes of the spinels
10 prepared according to Example 1 and Comparative Examples 1 and 2 are almost the same.

On the second x-axis of FIG. 5, the respective a-axis values for 2θ of the spinel unit cell in Å are shown. As shown in FIG. 5, the plane profiles
15 correspond to the lattice distortion distribution and the a-axis distribution in the final product. The data presented in FIG. 5 demonstrates that in the conventionally prepared spinel, according to Comparative Examples 1 and 2, numerous phases in which
20 a-axis value may vary in the range of 0.05 - 0.1 angstroms can simultaneously coexist. This distortion causes permanent internal stress in the crystallites and can be a source of fast crystallite deterioration during cycling when additional changes of the lattice
25 parameters take place.

FIG. 6 is a graph trace showing the variation of the a-axis of the unit cell parameters corresponding to the mean lithium/manganese ratio in the $\text{Li}_{1+x}\text{M}_{2-x}\text{O}_4$ compounds at a cooling rate of 100°C/h. The values in
30 FIGS. 5 and 6 provide the relationship between the lithium/manganese ratio and the value of 2θ shown in FIG. 7. In FIG. 7, the second x-axis illustrates the variation of the lithium/manganese ratio as it corresponds to the value of 2θ under the assumption
35 that the lattice distortion is caused only by the random distribution of the lithium-manganese ratio in the spinel compound. Based on this assumption, which

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may be true at a fixed oxygen content in the compound, the (400) reflection peak will correspond to the lithium/manganese ratio distribution in the spinel.

FIG. 8 is a diagram illustrating the concept that broad x-ray diffraction profiles, such as the ones corresponding to the spinel compounds of the comparative examples, may be considered as phase distribution curves of lithium spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ phases with different lithium/manganese ratios. The coexistence of the infinite sequences of high and low lithium content spinels with a general formula $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$, wherein X can have an infinite numbers of values, is illustrated in FIG. 6. From the x-ray diffraction profiles displayed in FIGS. 5 and 7 as a function of lithium/manganese ratio, it follows that the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ compounds with a broad full width at half maximum are most likely nonhomogeneous and can simultaneously contain considerably higher lithium content and lower lithium content spinel phases compared to the corresponding mean value spinel phases. In fact, during the firing process, spinels with lower lithium content than the stoichiometric ratio may be undesirably transformed into Mn_2O_3 and higher lithium content spinel phases by a disproportionation reaction. Analogously, the extremely high lithium content spinel phase may be undesirably transformed into Li_2MnO_3 and lower lithium content spinel phases by another disproportionation reaction. It is important to emphasize that both Mn_2O_3 and Li_2MnO_3 are not electrochemically active in the 4 V region and can exist in considerable amount as amorphous impurities in the final product. The existence of the Mn_2O_3 and Li_2MnO_3 impurities decrease both the specific capacity and the cycleability of the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ compound.

As illustrated herein, the full width at half maximum of the peaks of diffraction planes reflects to the lattice distortion, homogeneity, and impurity level

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of the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ compound. All of these parameters have a considerable impact on the spinel cycleability. The full width at half maximum values of the reflection (400) and (440) peaks are highly
5 reproducible and thus may be used as a reference for spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ electrochemical performance.

As described above, the spinel lattice distortion may be mainly due to random distortion caused by simultaneous existence of lithium rich and
10 lithium poor spinel phases and can be decreased by increasing the homogeneity of the lithium/manganese distribution in the final product. The highly uniform lithium/manganese distribution in the final product of the present invention provides a spinel having high
15 specific capacity and long cycling life.

FIG. 9 shows the dependence of discharge specific capacities on the charge-discharge cycle numbers of the spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ compounds of Example 1 and the comparative examples. As shown in FIG. 9,
20 spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compounds formed according to the present invention maintain their specific capacity after numerous cycles and therefore exhibit long cycling life.

It is understood that upon reading the above
25 description of the present invention, one skilled in the art could make changes and variations therefrom. These changes and variations are included in the spirit and scope of the following appended claims.

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THAT WHICH IS CLAIMED:

1. A method of preparing a spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ intercalation compound comprising:
 - (a) mixing at least one manganese compound
5 selected from the group consisting of manganese salts and manganese oxides with at least one lithium compound selected from the group consisting of lithium salts and lithium oxides;
 - (b) firing the mixture from step (a) to a
10 temperature of between about 400°C and 500°C in the presence of a gas flow with a flow rate of between about 0.5 l/gh and 5.0 l/gh to form an oxygen rich spinel;
 - (c) firing the oxygen rich spinel from step
15 (b) to a temperature of between 500°C and 600°C in the presence of a gas flow with a flow rate of between about 0.1 l/gh and 1.0 l/gh to form a distorted $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel; and
 - (d) firing the distorted spinel from step
20 (c) to a temperature of between 700°C and 800°C in the presence of a gas flow with a flow rate of between about 0.005 l/gh and 0.2 l/gh to form an ordered stoichiometric $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel.

2. A method of preparing a positive
25 electrode for an electrochemical cell comprising:
 - (a) mixing at least one manganese compound selected from the group consisting of manganese salts and manganese oxides with at least one lithium compound selected from the group consisting of lithium salts and
30 lithium oxides;
 - (b) firing the mixture from step (a) to a temperature of between about 400°C and 500°C in the presence of a gas flow with a flow rate of between about 0.5 l/gh and 5.0 l/gh to form oxygen rich
35 spinels;

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(c) firing the oxygen rich spinels from step (b) to a temperature of between 500°C and 600°C in the presence of a gas flow with a flow rate of between about 0.1 l/gh and 1.0 l/gh to form distorted $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinels;

(d) firing the distorted $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinels from step (c) to a temperature of between 700°C and 800°C in the presence of a gas flow with a flow rate of between about 0.005 l/gh and 0.2 l/gh to form ordered $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinels;

(e) dispersing the ordered $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinels in a solvent with a conductive agent and a binder material to form a slurry;

(f) heating the slurry to evaporate the solvent to form a dry electrode;

(g) compressing the dry electrode; and

(h) cutting the dry electrode to form a positive electrode for an electrochemical cell.

3. The method according to Claims 1 or 2 further comprising cooling the ordered $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel after step (d) at a rate of greater than about 20°C per hour in the presence of a gas flow with a flow rate of between about 0 l/gh and 1.0 l/gh.

4. The method according to Claims 1 or 2 wherein the at least one manganese compound and the at least one lithium compound in step (a) are mixed in a lithium to manganese mole ratio of between about 1.02:2 and 1.1:2.

5. The method according to Claims 1 or 2 wherein firing steps (b), (c), and (d) are performed consecutively without cooling the spinel material between steps.

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6. The method according to Claims 1 or 2 wherein the firing temperature in step (b) is maintained for at least about four hours, the firing temperature in step (c) is maintained for at least
5 about ten hours, and the firing temperature in step (d) is maintained for at least about ten hours.

7. The method according to Claims 1 or 2 wherein the at least one manganese compound is selected from the group consisting of MnO_2 , Mn_2O_3 , Mn_3O_4 , $MnCO_3$,
10 $MnSO_4$, $Mn(NO_3)_2$, $Mn(CH_3CO_2)_2$, or mixtures thereof.

8. The method according to Claims 1 or 2 wherein the at least one lithium compound is selected from the group consisting of Li_2O , $LiOH$, $LiNO_3$, Li_2CO_3 , Li_2SO_4 , $LiNO_3$, $LiCH_3CO_2$, or mixtures thereof.

15 9. The method according to Claims 1 or 2 wherein the gas in said firing steps is selected from the group consisting of air and a gas mixture having an oxygen content of between about 5 and 100% oxygen by volume.

20 10. A spinel $Li_{1+x}Mn_{2-x}O_4$ intercalation compound prepared according to the method of Claims 1 or 2.

11. An electrochemical cell comprising a spinel $Li_{1+x}Mn_{2-x}O_4$ intercalation compound prepared
25 according to the method of Claims 1 or 2.

12. A $Li_{1+x}Mn_{2-x}O_4$ spinel having a mean X value of between about 0.01 to 0.05 and a full width at half maximum of the x-ray diffraction peaks at a diffraction angle 2θ of planes (400) and (440) using $CuK\alpha_1$ rays of
30 between about 0.10° and 0.15° .

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13. A positive electrode for an electrochemical cell comprising:

5 a $\text{Li}_{1-x}\text{Mn}_{2-x}\text{O}_4$ spinel having a mean X value of between about 0.01 to 0.05 and a full width at half maximum of the x-ray diffraction peaks at a diffraction angle 2θ of planes (400) and (440) using $\text{CuK}\alpha_1$ rays of between about 0.10° and 0.15° ;

a conductive agent; and

a binder material.

10 14. The product according to Claims 12 or 13, wherein the mean crystallite size of the $\text{Li}_{1-x}\text{Mn}_{2-x}\text{O}_4$ spinel is between about 3,000 and 30,000 angstroms.

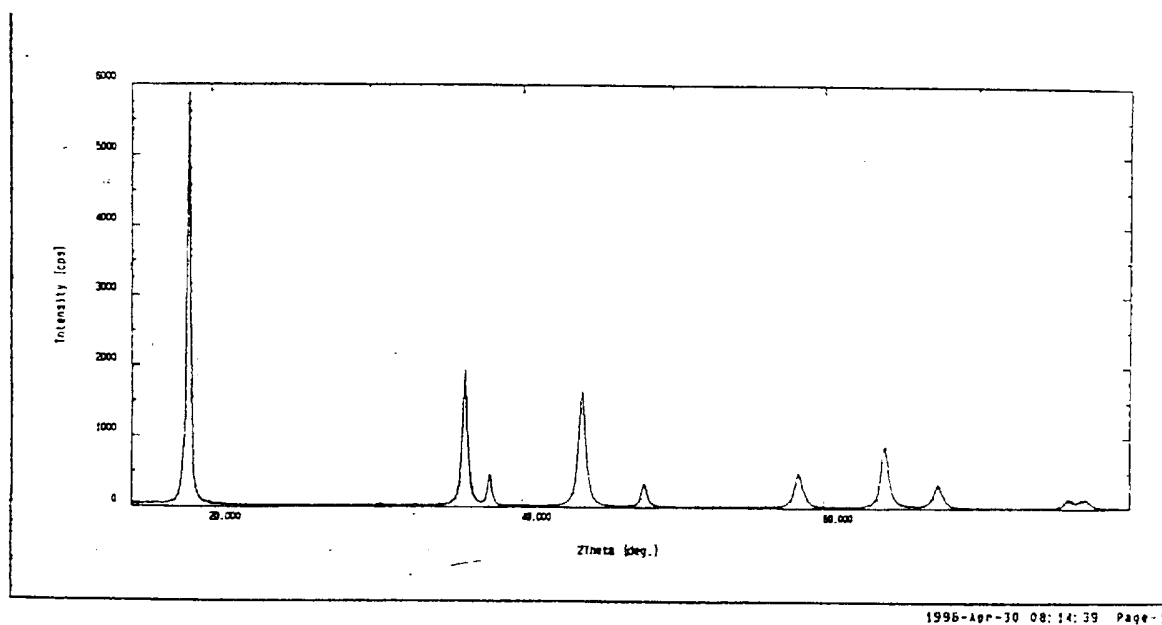


FIG. 1

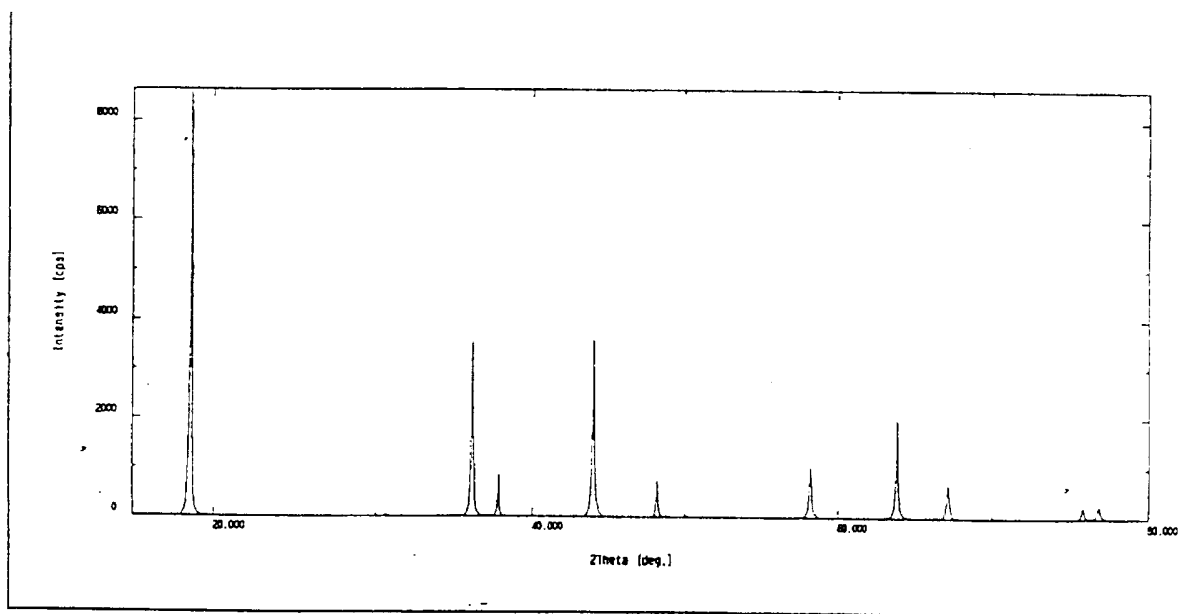


FIG. 2

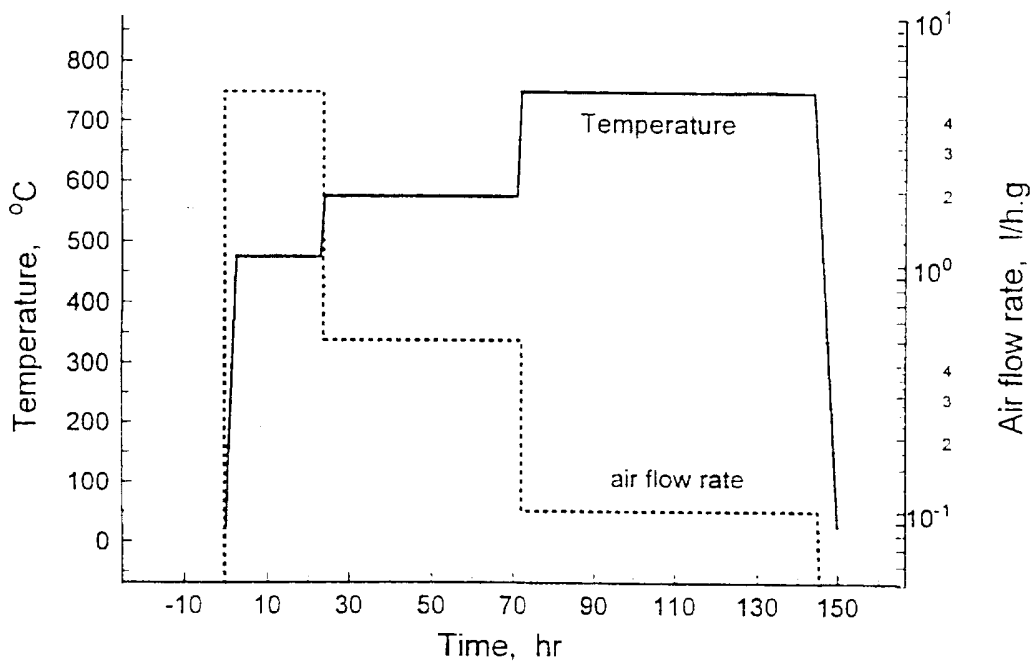
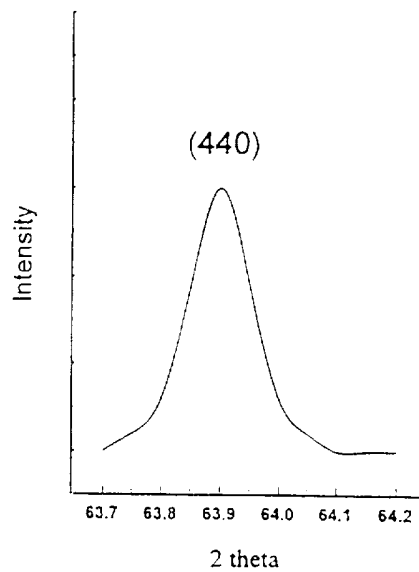
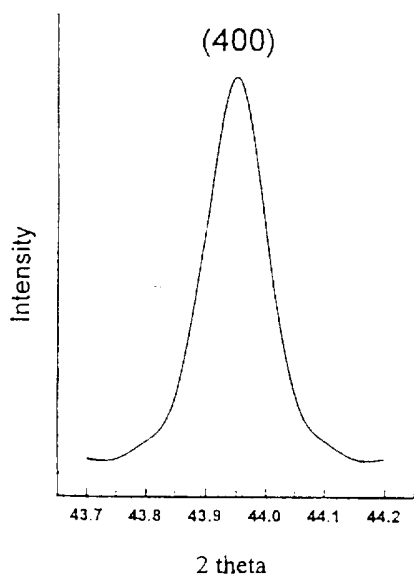


FIG. 3



FIGS. 4A AND 4B

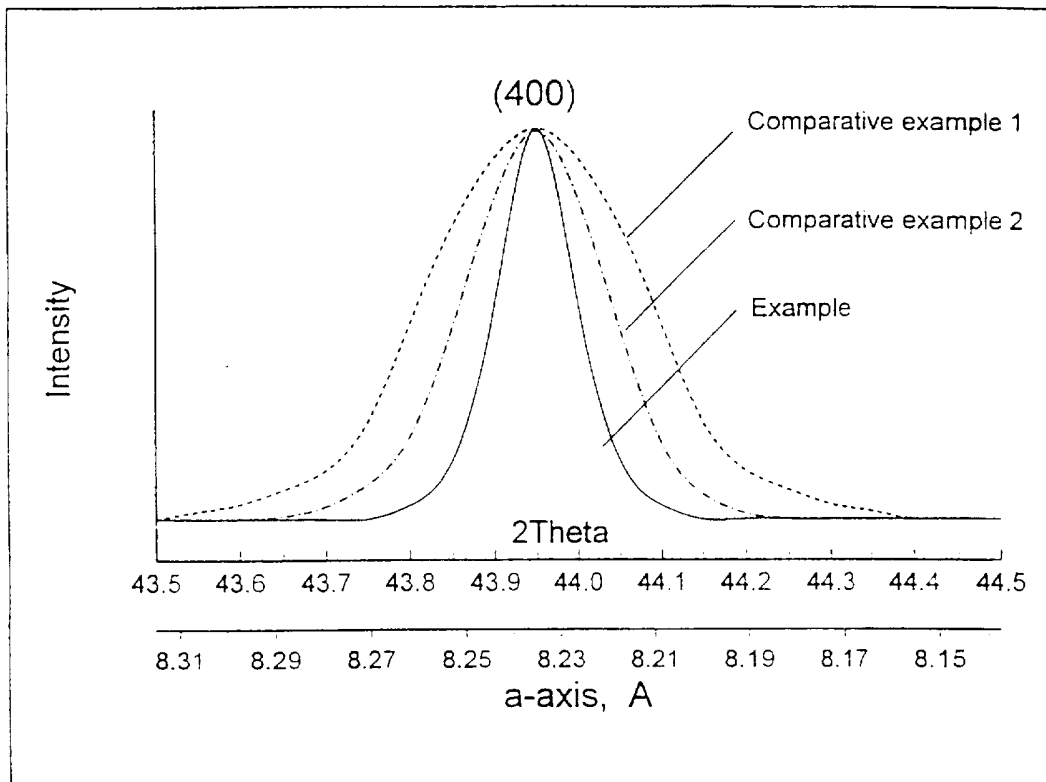


FIG. 5

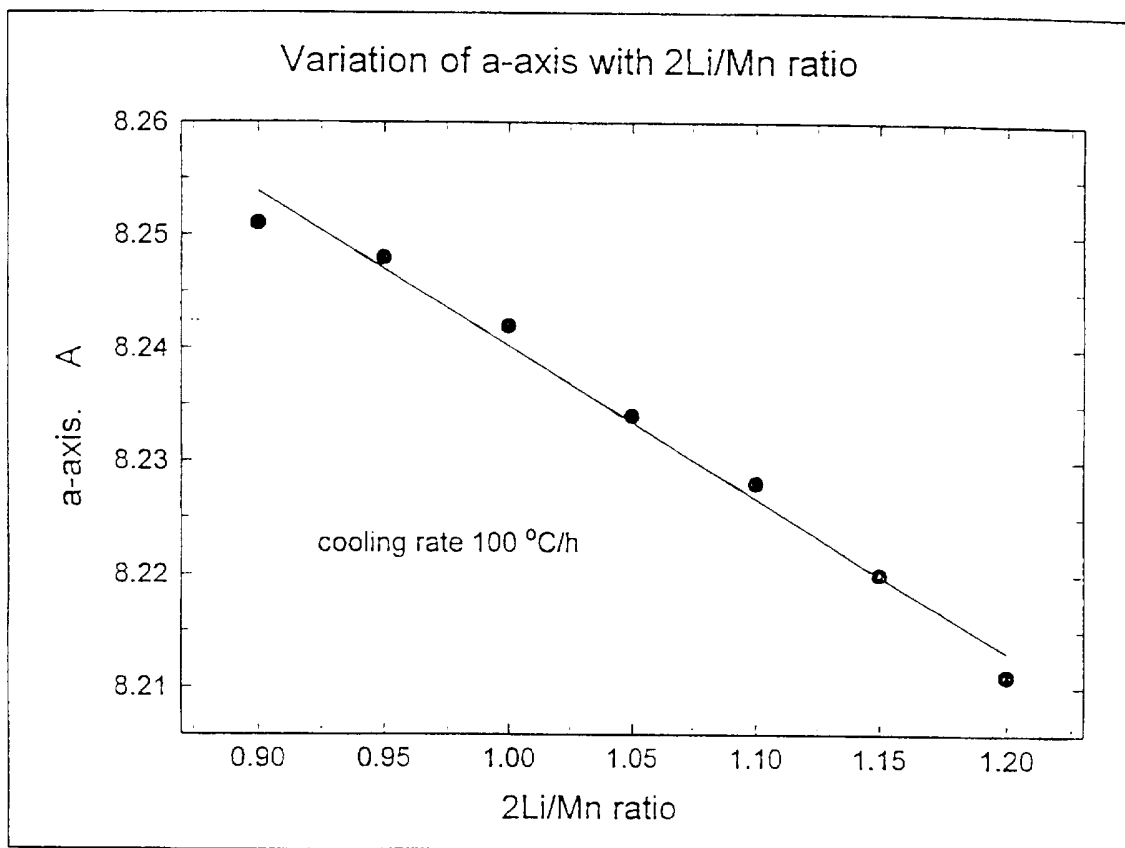


FIG. 6

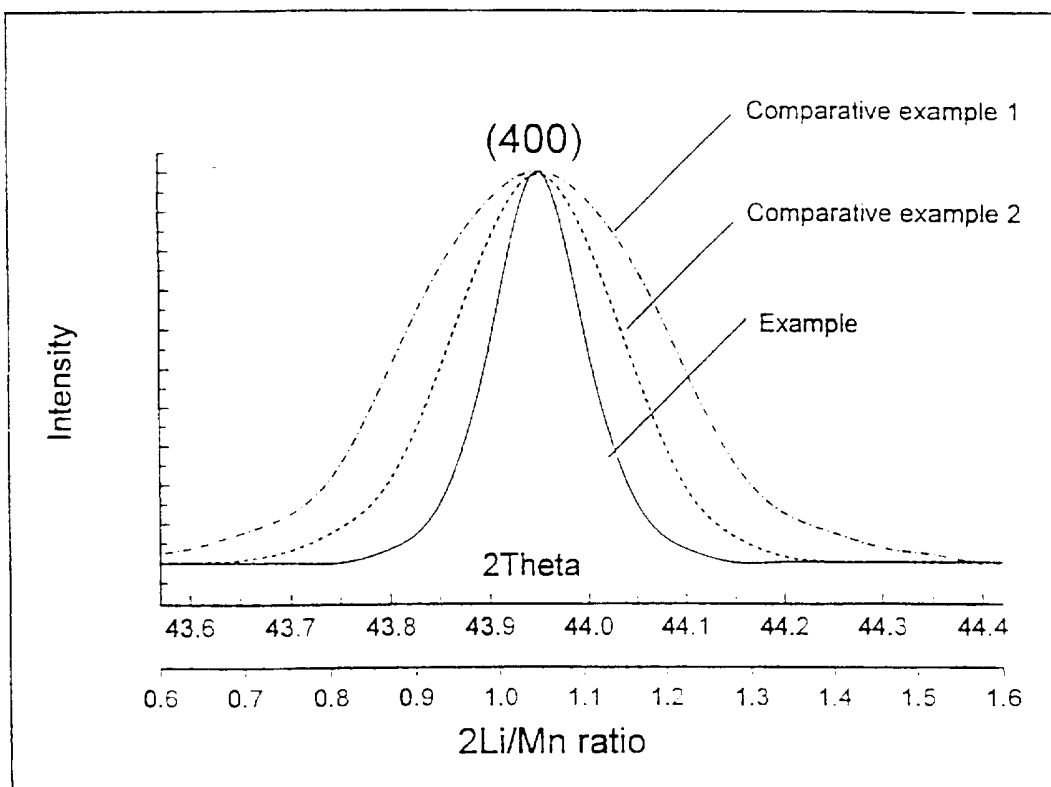


FIG. 7

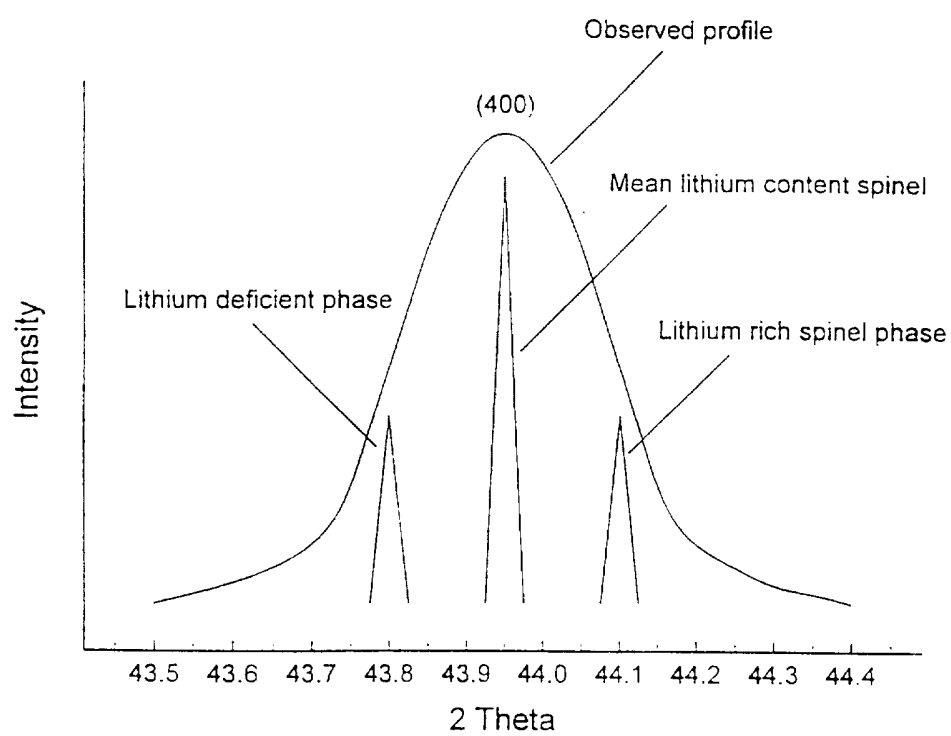


FIG. 8

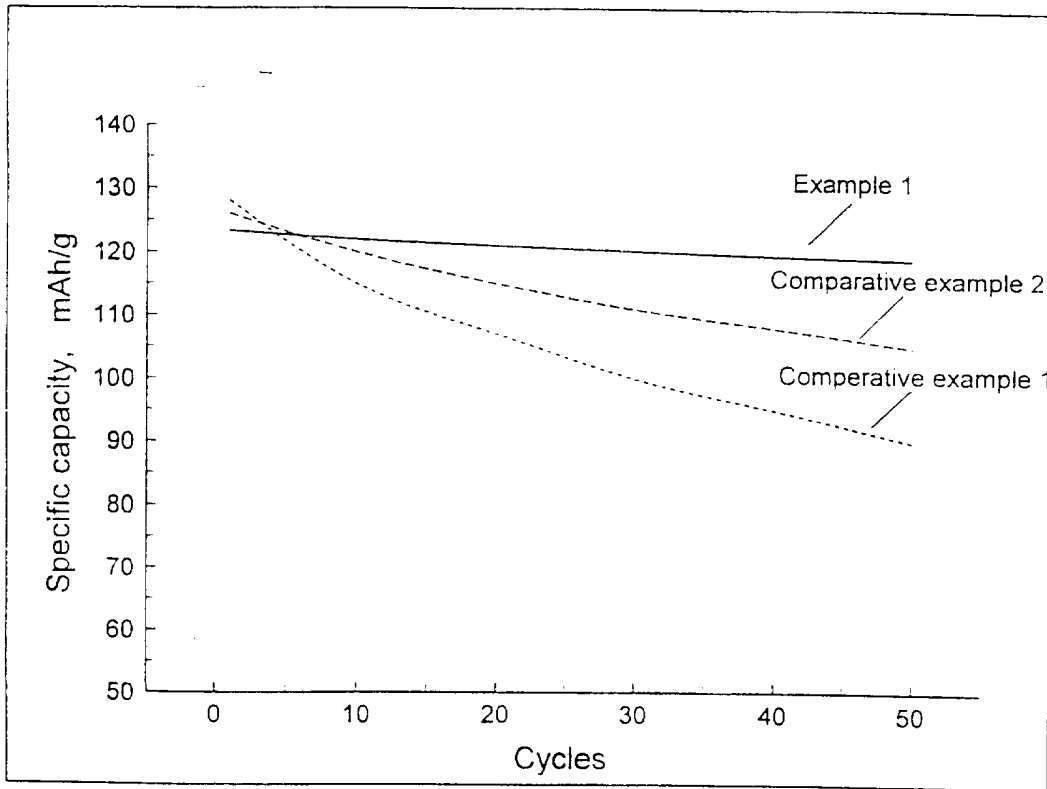


FIG. 9

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/19152

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01G45/00 H01M4/50

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.
A	EXTENDED ABSTRACTS, vol. 95/2, 1 January 1995, page 126/127 XP000553867 YUAN GAO ET AL: "CHARACTERIZING LI1+XMN2-XO4 FOR LI-ION BATTERY APPLICATIONS" see the whole document ---	1,9
P,A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 143, no. 1, 1 January 1996, pages 100-114, XP000556212 GAO Y ET AL: "SYNTHESIS AND CHARACTERIZATION OF LI1+XMN2-XO4 FOR LI-ION BATTERY APPLICATIONS" see page 100 - page 101 --- -/--	1,3,6-9, 12

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

25 March 1997

Date of mailing of the international search report

02.04.97

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/19152

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MATERIALS RESEARCH BULLETIN, vol. 25, no. 2, 1 February 1990, pages 173-182, XP000161192 ROSSOUW M H ET AL: "STRUCTURAL ASPECTS OF LITHIUM-MANGANESE-OXIDE ELECTRODES FOR RECHARGEABLE LITHIUM BATTERIES" see the whole document ---	1,4,6-8, 12
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International Application No

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