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 4/50

A1

(11) International Publication Number: WO 97/37935

(43) International Publication Date: 16 October 1997 (16.10.97)

(21) International Application Number: PCT/US97/05550

(22) International Filing Date: 2 April 1997 (02.04.97)

(30) Priority Data:

60/015,143	5 April 1996 (05.04.96)	US
08/756,496	26 November 1996 (26.11.96)	US

(60) Parent Application or Grant
(63) Related by Continuation
US 08/756,496 (CON)
Filed on 26 November 1996 (26.11.96)

(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). EBNER, Walter [US/US]; 2896 Colony Woods Drive, Gastonia, NC 28054 (US). THOMPSON, William [US/US]; 1514 Village Court, Gastonia, NC 28054 (US). DOW, Stephen [US/US]; 1800-F Yellowstone Court, Gastonia, NC 28054 (US).

(74) Agents: LINKER, Raymond, O., Jr. et al.; Bell, Seltzer, Park & Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US).

(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 (GH, 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).

Published
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.

(54) Title: METHOD FOR PREPARING SPINEL $Li_{1+X}Mn_{2-X}O_{4+Y}$ INTERCALATION COMPOUNDS

(57) Abstract

A novel method of preparing a highly homogeneous spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compound having a predetermined mean particle size and particle size distribution for 4 V secondary lithium and lithium ion cells is provided. The method comprises mixing at least one manganese compound having a predetermined particle size distribution with at least one lithium compound wherein the manganese compound has a mean particle size of between about 1 and 15 microns and the mean particle size of the lithium compound is less than that of the manganese compound. The mixture is then fired in one or more firing steps within specific temperature ranges to form the $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compound. Preferably, at least one firing step is at a temperature of between about 700 °C and 900 °C. The $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds may be used in the positive electrodes of secondary lithium and lithium ion cells to provide cells having high specific capacity, cycleability, and charge-discharge rate capability.

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

METHOD FOR PREPARING SPINEL $Li_{1+X}Mn_{2-X}O_{4+Y}$ INTERCALATION COMPOUNDS

FIELD OF THE INVENTION

This invention relates to spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds, and particularly to the use of spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds in 4 V secondary lithium and lithium ion batteries.

BACKGROUND OF THE INVENTION

Heretofore, lithium intercalation compounds such as $Li_{1+X}Mn_{2-X}O_{4+Y}$ have been used in positive electrodes for 4 V secondary lithium and lithium ion batteries. The spinel $LiMn_2O_4$ intercalation compound was first obtained by Wickham and Croft by heating lithium carbonate and manganese oxide in a 1:2 lithium to manganese molar ratio. D. G. Wickham and W. J. Croft, *Crystallographic and Magnetic Properties of Several Spinels Containing Trivalent JA-1044 Manganese*; J. Phys. Chem. Solids **7**, 351-360 (1958). As demonstrated in U.S. Pat. No. 4,426,253 to Hunter, the acid treatment of $LiMn_2O_4$ forms a λ-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., *Lithium Insertion Into Manganese Spinels*; Material Research Bulletin **18**, 461-472 (1983).

The mean particle size and the particle size distribution are two of the basic properties characterizing the positive electrode intercalation materials for secondary lithium batteries. These properties are considered to be important because they directly influence the charge-discharge rate capability, the safety cell performance, the electrode formulation and the electrode coating process of positive electrodes containing these materials. In addition, a decrease in the mean particle size and distribution of the intercalation compounds typically results in an increase in the cycleability of these compounds. The reason for the increase in cycleability is that smaller particles are relatively more flexible than larger particles and therefore the changes in the crystal lattice parameters which occur during cycling do not damage the cycleability of the smaller particles to the degree that the larger particles are damaged.

Nevertheless, a decrease in the mean particle size results in a significant increase in the electronic resistivity of the spinel compounds. The electronic resistivity is controlled by the contact resistivity between the particles which rises significantly due to an increase in the number of contact boundaries which the electrons have to overcome. The increase in electronic resistivity leads to an increase in the electrode polarization which decreases both the specific capacity and charge-discharge rate capability of the electrode. Furthermore, a decrease in the particle size is generally coupled with an unwanted decrease in the tapped or powder density. Because many batteries such as batteries for electronics have fixed volumes, it is preferred that the spinel material used in the positive electrode of these batteries has a high tapped density, so there is essentially more chargeable material in the positive electrode. A higher tapped density results in a positive electrode having a higher overall capacity. Therefore, depending on the nature of the intercalation compounds and the electrode formulation, the cycleability, specific capacity, tapped density and charge-discharge rate of the spinel material should be considered in determining a desirable particle distribution for the spinel material.

Accordingly, these factors have been considered in the preparation of $LiCoO_2$ intercalation compounds, where the desired particle size has been achieved by grinding the $LiCoO_2$ material. Nevertheless, grinding $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds results in a considerable reduction in specific capacity. V. Manev et al., *Rechargeable Lithium Battery With Spinel-Related λ-MnO_2. Part III. Scaling-up Problems Associated With $LiMn_2O_4$ Synthesis*, J. Power Sources 54, 323-328 (1995). As described in this article, the reduction in specific capacity is due to changes in the $Li_{1+X}Mn_{2-X}O_{4+Y}$ structure which occur as a result of the stress of mechanical treatment, measured by the contraction of the crystal lattice parameter *a*. Therefore, grinding the $Li_{1+X}Mn_{2-X}O_{4+Y}$ material is not a desirable method of reducing the mean particle size and particle size distribution of spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds.

SUMMARY OF THE INVENTION

The present invention provides a method of preparing a spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compound having a predetermined mean particle size and particle distribution for 4 V secondary lithium and lithium ion cells having high cycleability, specific capacity, and charge-discharge rate capability.

The method of preparing the spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compound comprises mixing at least one manganese compound with at least one lithium compound and firing the mixture in one or more steps within specific temperature ranges. The temperature ranges of the firing steps fall between about 450°C and 900°C with at least one firing step at a temperature of between about 700°C and 900°C to form the $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compound. Typically, the mean particle size of the lithium compound used to form the spinel is less than the mean particle size of the manganese compound thereby allowing the lithium particles to be uniformly dispersed with the manganese particles. Preferably, the manganese compound used to form the spinels has a predetermined mean particle diameter of between about 1 and 15 microns and a predetermined particle size distribution wherein at least about 99% of the particles have a diameter of less than about 40 microns. In addition, the manganese compounds preferably have a narrow particle size distribution wherein the maximum particle diameter is less than about 10 times the mean particle diameter and/or at least about 90% of the particles are distributed in a range not wider than about one order of magnitude.

The spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds prepared according to the present invention have a predetermined mean particle size and particle size distribution generally corresponding to the size of the particles in the manganese compounds. Therefore, the predetermined mean particle size and particle size distribution is achieved without any additional mechanical treatment, e.g., grinding, of the spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ compounds. The $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds may be used in the positive electrodes of secondary lithium and lithium ion cells to provide cells having high cycleability, specific capacity and charge-discharge rate capability.

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 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 a graph illustrating the comparison between the particle size distributions of the starting MnO_2 and the spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ mixture obtained from firing a mixture of the MnO_2 and LiOH at 750°C for 48 hours.

FIG. 2 is a graph illustrating the comparison between the particle size distributions of the starting MnO_2 and the spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ compound obtained from firing a mixture of the MnO_2 and Li_2CO_3 at 850°C for 48 hours.

FIG. 3 is a graph illustrating the comparison between the particle size distributions of the starting $MnCO_3$ and the spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ compound obtained from firing a mixture of the $MnCO_3$ and $LiNO_3$ at 750°C for 48 hours.

FIG. 4 is a graph illustrating the comparison between the particle size distribution of a spinel prepared according to the invention and a spinel prepared from a lithium compound having a larger mean particle size according to a comparative example.

FIG. 5 is a graph illustrating the comparison between the particle size distribution of a spinel prepared according to the present invention and the same spinel compound ground for about 10 minutes in a ball mill according to a comparative example.

DETAILED DESCRIPTION OF THE INVENTION

It has been discovered that according to the method of the present invention, spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ material having a predetermined mean particle size and a narrow particle distribution may be prepared without further mechanical treatment and losses in specific capacity, cycleability, tapped density and charge-discharge rate capability. The spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ material is prepared from a starting mixture which includes at least one manganese compound and at least one lithium 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, $MnCO_3$, $MnSO_4$, $Mn(NO_3)_2$, MnOOH, $Mn(CH_3CO_2)_2$, and mixtures thereof. The at least one lithium compound is selected from the group consisting of lithium salts and lithium oxides. Exemplary lithium 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 of between about 1.02:2 and 1.1:2.

In order to provide highly homogenous spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds having a predetermined mean particle size and narrow particle size distribution, the particle size of the starting materials, specifically the manganese compound is controlled. The manganese compound has a predetermined mean particle diameter of between about 1 and 15 microns, preferably between greater than 1 to about 15 microns and more preferably between about 5 and 15 microns, and a predetermined particle size distribution wherein at least about 99% of the particles have a diameter of less than about 40 microns. Additionally, the maximum particle diameter of the manganese compound is typically less than about 10 times the mean particle diameter and preferably less than about 5 times the mean particle diameter. The manganese compound is preferably highly homogenous wherein at least about 90% of the manganese compound particles are distributed in a range not wider that about one order of magnitude. The manganese compound may be ground such as by a ball or jet mill to provide the desired particle size used in the invention.

The lithium compound used to form the spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds of the present invention typically has a smaller mean particle size than the manganese compound used. Preferably, the mean particle size of the lithium compound is at least two to three times lower than that of the manganese compound. The smaller particle size lithium compounds become more uniformly dispersed with the manganese compound particles upon mixing to provide more homogenous spinel compounds with increased cycling lives. Preferably, the mean particle size of the lithium compound is between about 0.5 and 5 microns, more preferably between about 1 and 3 microns. The lithium compound may be ground such as by a ball or jet mill to provide the desired particle size used in the invention. However, the lithium compound and manganese compound are preferably ground separately to provide a lithium compound having a smaller mean particle size than that of the manganese compound used in the invention.

In order to form the spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds, the at least one manganese compound having a predetermined particle size and particle distribution and the at least one lithium compound having a predetermined mean particle size less than that of the manganese compound are mixed together and fired in one or more steps within specific temperature ranges which fall between 450°C and 900°C. Preferably, at least one firing step is at a temperature of between about 700°C and 900°C. In this firing step, the temperature is maintained between about 700°C and 900°C for a soak time of at least about 10 hours, and preferably for at least about 24 hours, to form the spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ material. In order to provide a spinel having enhanced properties, the mixture may be subjected to an additional firing step at a temperature range of between about 400°C and 600°C for at least about 12 hours prior to the 700°C-900°C firing step. Additionally, the mixture is generally fired in the presence of a gas flow such as air or a gas mixture containing from 5 to 100 percent oxygen by volume. Suitable firing step sequences are described in commonly owned applications entitled "Highly Homogenous Spinel $Li_{1+X}Mn_{2-X}O_4$ Intercalation Compounds and Method for Preparing Same", Serial Nos. 08/665,396 and 08/665,408, filed concurrently on June 18, 1996 and incorporated herein in their entirety by reference.

Any of the firing steps used to form the spinel may include changes in the temperature within the described ranges. In other words, the temperature may be increased or decreased within the described ranges during the firing step. 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 soak times are typically dictated by commercial feasibility and extremely long soak times may not be desired.

In accordance with one aspect of the present invention a spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ with strictly defined particle size and particle size distribution is provided by firing a reaction mixture of the manganese compound and the lithium compound in one or more firing steps with at least one firing step at a temperature of between about 700°C and 800°C, preferably between about 730°C and 770°C, and more preferably up to about 750°C. In this temperature range, the particle size distribution of the final $Li_{1+X}Mn_{2-X}O_{4+Y}$ essentially corresponds to the particle size distribution of the starting manganese compound.

In accordance with another aspect of the present invention, a spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ with controlled particle size and particle size distribution is provided by firing a reaction mixture of the manganese compound and the lithium compound in one or more firing steps with at least one firing step at a temperature of between about 800°C and 900°C, preferably between about 800°C up to about 850°C, and more preferably about 825°C. In this temperature range, the particle size distribution of the $Li_{1+X}Mn_{2-X}O_{4+Y}$ spinel material is directly related to the particle size distribution of the starting manganese compound. Nevertheless, in this temperature range, there is generally an offset between the particle size distribution of the $Li_{1+X}Mn_{2-X}O_{4+Y}$ material and the particle size distribution of the starting manganese compound corresponding to an increase in the particle size of the spinel material at the higher temperature range. For example, the mean particle size of the spinel is between about 10 and 15 microns when the mean particle size of the manganese compound is between about 6 and 7 microns when the starting materials are fired at between about 800°C and 900°C. In both the low temperature range (700°C-800°C) and the high temperature range (800°C-900°C), the $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds are highly homogenous and possess a high specific capacity, cycleability, tapped density and charge-discharge rate capability.

The spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compounds prepared according to the present invention possess improved properties over conventional $Li_{1+X}Mn_{2-X}O_{4+Y}$ spinels. The spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ of the invention is a highly ordered and homogeneous structure having a low capacity fade during cycling. The improved physicochemical and electrochemical properties of the $Li_{1+X}Mn_{2-X}O_{4+Y}$ spinels of the invention are independent of the specific manganese and lithium compounds used to form the spinel but are dependent instead on the particle size of the manganese and lithium compounds.

The spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ compounds may be used in positive electrodes in electrochemical cells. The $Li_{1+X}Mn_{2-X}O_{4+Y}$ 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 an aluminum current collector 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.

EXAMPLE 1

Chemical grade MnO_2 particles were subjected to preliminary grinding until a mean particle size of 2 microns was obtained. The $Li_{1.025}Mn_{1.975}O_4$ sample was produced by heating a 500 g mixture of the ground MnO_2 and LiOH at a molar ratio 2Li:Mn = 1.05. The mixture was then fired for 48 h at 750°C in a muffle furnace. The spinel material was cooled by removing the material from the furnace.

The effect of the particle size distribution of the starting MnO_2 having a mean particle size of 2 microns on the particle size distribution of the $Li_{1.025}Mn_{1.975}O_4$ is illustrated in FIG. 1. FIG. 1 shows that the particle size distributions of the MnO_2 starting material and the final $Li_{1.025}Mn_{1.975}O_4$ correspond remarkably well.

EXAMPLE 2

The MnO_2 used in Example 1 was mixed with $LiCO_3$ at a molar ratio 2Li:Mn = 1.1 and fired for 48 h at 850°C in a muffle furnace. The spinel material was cooled by removing the spinel material from the furnace.

The effect of the particle size distribution of the starting MnO_2 having a mean particle size of 2 microns on the particle size distribution of the final $Li_{1.05}Mn_{1.95}O_4$ is illustrated in FIG. 2. As shown in FIG. 2, firing the MnO_2 and $LiCO_3$ at 850°C shifts the particle size distribution curve of the $Li_{1.05}Mn_{1.95}O_4$ spinel particles to higher values than those obtained using the 750° firing. Despite the higher particle size resulting from 850°C firing, the distribution transforms into an even more symmetrical distribution curve with the maximum particle size of the final product slightly exceeding the maximum particle size of the starting manganese compound. Therefore, as with the material fired at 750°C in Example 1, the particle size and particle size distribution can be defined by particle size distribution curve of the starting compound and by calculation of the offset of the distribution curves after the firing on the basis of the preliminarily obtained experimental data.

EXAMPLE 3

$MnCO_3$ was subjected to preliminary grinding until a compound with mean particle size of 9 microns was obtained. The $Li_{1.025}Mn_{1.975}O_4$ sample was produced by heating a 500 g mixture of the ground $MnCO_3$ and $LiNO_3$ at a molar ratio of 2Li:Mn = 1.05. The mixture was fired for 48 h at 750°C in a muffle furnace. The synthesized spinel was cooled by removing the spinel material from the furnace.

Even though a small difference is observed in FIG. 3 in the particle size distribution of the starting $MnCO_3$ and the final spinel $Li_{1.025}Mn_{1.975}O_4$, the difference between the mean particle size of these materials is negligible. The comparison between the mean particle diameters of the starting $MnCO_3$, (8.49 microns) and the mean diameter of the final spinel $Li_{1.025}Mn_{1.975}O_4$, (8.88 microns) shows only a 4.5% change from the initial value of the manganese compound.

EXAMPLE 4

The $Li_{1.025}Mn_{1.975}O_4$ sample was produced by heating a 500 g mixture of the $MnCO_3$ in Example 3 and Li_2CO_3 with a mean particle size of 2.5 microns at a molar ratio of 2Li/Mn = 1.05. After a preliminary treatment at 550°C and 750°C, the mixture was fired at 850°C for 48 hours in a muffle furnace. The synthesized spinel was cooled at a cooling rate of 50°C/hour.

The prepared spinel $Li_{1.025}Mn_{1.975}O_4$ compound was mixed with 10% graphite and 5% PVDF binder dissolved in NMP solvent to form a slurry. The slurry was spread on aluminum foil and 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 EC:DMC/$LiPF_6$ electrolyte and a charging-discharging test was conducted at 1 h charge-discharge rate and 3 - 4.5 V voltage limits.

COMPARATIVE EXAMPLE 1

The $Li_{1+X}Mn_{2-X}O_{4+Y}$ sample was produced by heating a 500 g mixture of the $MnCO_3$ in Example 3 and Li_2CO_3 with a mean particle size of 36 microns at a molar ratio of 2Li/Mn = 1.05. The synthesis conditions were exactly the same as in Example 4, where after a preliminary treatment at 550°C and 750°C, the mixture was fired for 48 hours at 850°C in a muffle furnace. The synthesized spinel was cooled at a cooling rate of 50°C/hour. A spinel $Li_{1.025}Mn_{1.975}O_4$ positive test electrode was prepared in the same manner as in Example 4, an electrochemical cell was assembled in the same manner as in Example 4, and the cell charge-discharge characteristics were measured under the same conditions as Example 4.

COMPARATIVE EXAMPLE 2

The $Li_{1.025}Mn_{1.975}O_4$ sample was prepared by grinding the spinel $Li_{1.025}Mn_{1.975}O_4$ compound described in Example 4 in a ball mill for about 10 minutes. A spinel $Li_{1.025}Mn_{1.975}O_4$ positive test electrode was prepared in the same manner as in Example 4, an electrochemical cell was assembled in the same manner as in Example 4, and the cell charge-discharge characteristics were measured under the same conditions as Example 4.

The comparison between the particle size distribution of the spinel compound prepared according to Example 4 and Comparative Example 1 is illustrated in Fig. 4. Fig. 4 demonstrates that the particle size of the lithium compound, which differs in the two examples by more than one order of magnitude, does not have any effect on the particle size distribution of the final spinel compound. However, as shown in Table 1 below, the comparison between the cycleability of the spinel compounds prepared according to the Example 4 and Comparative Example 1 demonstrates that the cycleability of the spinel prepared by using a lithium compound with a smaller particle size than the manganese compound is considerably better than the cycleability of the spinel prepared by using a lithium compound with a larger particle size than the manganese compound. Specifically, after fifty cycles, the specific capacity of the spinel in Example 4 decreases only 2.4% compared to 8.1% for Comparative Example 1.

TABLE 1

Specific capacity (mAh/g)			
	First Cycle	Twentieth Cycle	Fiftieth Cycle
EXAMPLE 4	123	121	120
COMPARATIVE EXAMPLE 1	124	117	114

The comparison between the particle size distribution of the spinel prepared according to Example 4 and the particle size distribution curve of the ground spinel according to Comparative Example 2 is illustrated in Fig. 5. Fig. 5 shows a negligible decrease in the particle size distribution after the grinding procedure. In contrast, Table 2 demonstrates the comparison between the specific capacity of the spinels after numerous cycles. As shown in Table 2, both the initial specific capacity and the cycleability of the spinel is considerably decreased after grinding the spinel particles. In particular, the specific capacity of Example 4 after fifty cycles decreases only 2.4% compared to 11.8% for Comparative Example 2. This shows that grinding of the final spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ results in a strong negative effect on its electrochemical performance.

TABLE 2

Specific capacity (mAh/g)			
	First Cycle	Twentieth Cycle	Fiftieth Cycle
EXAMPLE 4	123	121	120
COMPARATIVE EXAMPLE 2	119	110	105

It is understood that upon reading the above 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.

CLAIMS:

1. A method of preparing a spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compound comprising:

mixing at least one manganese compound selected from the group consisting of manganese salts and oxides with at least one lithium compound selected from the group consisting of lithium salts and oxides, wherein the manganese compound consists of particles having a mean particle diameter of between about 1 and 15 microns; and

firing the mixture from the mixing step in one or more steps within specific temperature ranges to form the spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compound wherein at least one step is at a temperature of between about 700°C and 900°C.

2. A method of preparing a positive electrode for an electrochemical cell comprising:

(a) mixing at least one manganese compound selected from the group consisting of manganese salts and oxides with at least one lithium compound selected from the group consisting of lithium salts and oxides, wherein the manganese compound consists of particles having a mean particle diameter of between about 1 and 15 microns;

(b) firing the mixture from the mixing step in one or more steps within specific temperature ranges to form the spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compound wherein at least one step is at a temperature of between about 700°C and 900°C;

(c) dispersing the $Li_{1+X}Mn_{2-X}O_{4+Y}$ spinels in a solvent with a conductive agent and a binder material to form a slurry;

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

(e) compressing the dry electrode; and

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

3. The method according to claims 1 or 2 wherein the firing step comprises firing the mixture for a period of at least about 10 hours.

4. The method according to claims 1 or 2 wherein the firing step comprises firing the mixture for a period of at least about 24 hours.

5. The method according to claims 1 or 2 wherein the firing step comprises firing the mixture at a temperature of between about 700°C and 800°C.

6. The method according to claims 1 or 2 wherein the firing step comprises firing the mixture at a temperature of between about 800°C and 900°C.

7. The method according to claims 1 or 2 wherein the manganese compound particles of the mixing step have a maximum particle diameter of not greater than about 10 times the mean particle diameter.

8. The method according to claims 1 or 2 wherein at least about 99% of the manganese compound particles has a particle diameter of not greater than about 40 microns.

9. The method according to claims 1 or 2 wherein at least about 90% of the manganese compound particles are distributed in a range not wider than about one order of magnitude.

10. The method according to claims 1 or 2 wherein the firing step comprises firing the mixture at a temperature of between about 730°C and 770°C.

11. The method according to claims 1 or 2 wherein the firing step comprises firing the mixture at a temperature of between about 800°C and 850°C.

12. The method according to claims 1 or 2 wherein the manganese compound is selected from the group consisting of MnO_2, Mn_2O_3, Mn_3O_4, $MnCO_3$, $MnSO_4$, $Mn(NO_3)_2$, MnOOH, $Mn(CH_3CO_2)_2$, or mixtures thereof.

13. The method according to claims 1 or 2 wherein the 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.

14. The method according to claims 1 or 2 wherein the mean particle size of the lithium compound is less than the mean particle size of the manganese compound.

15. The method according to claim 14 wherein the mean particle size of the lithium compound is between about 0.5 and 5 microns.

16. The method according to claims 1 or 2 further comprising grinding the manganese compound prior to said mixing step.

17. A product prepared according the methods of claims 1 or 2.

18. A spinel $Li_{1+X}Mn_{2-X}O_{4+Y}$ intercalation compound having a mean particle size of between about 5 and 20 microns.

19. A positive electrode for an electrochemical cell comprising:

a $Li_{1+X}Mn_{2-X}O_{4+Y}$ spinel having a mean particle size of between about 5 and 20 microns;

a conductive agent; and

a binder.

20. The product according to claims 18 or 19 wherein the mean particle size of the spinel is between about 10 and 15 microns.

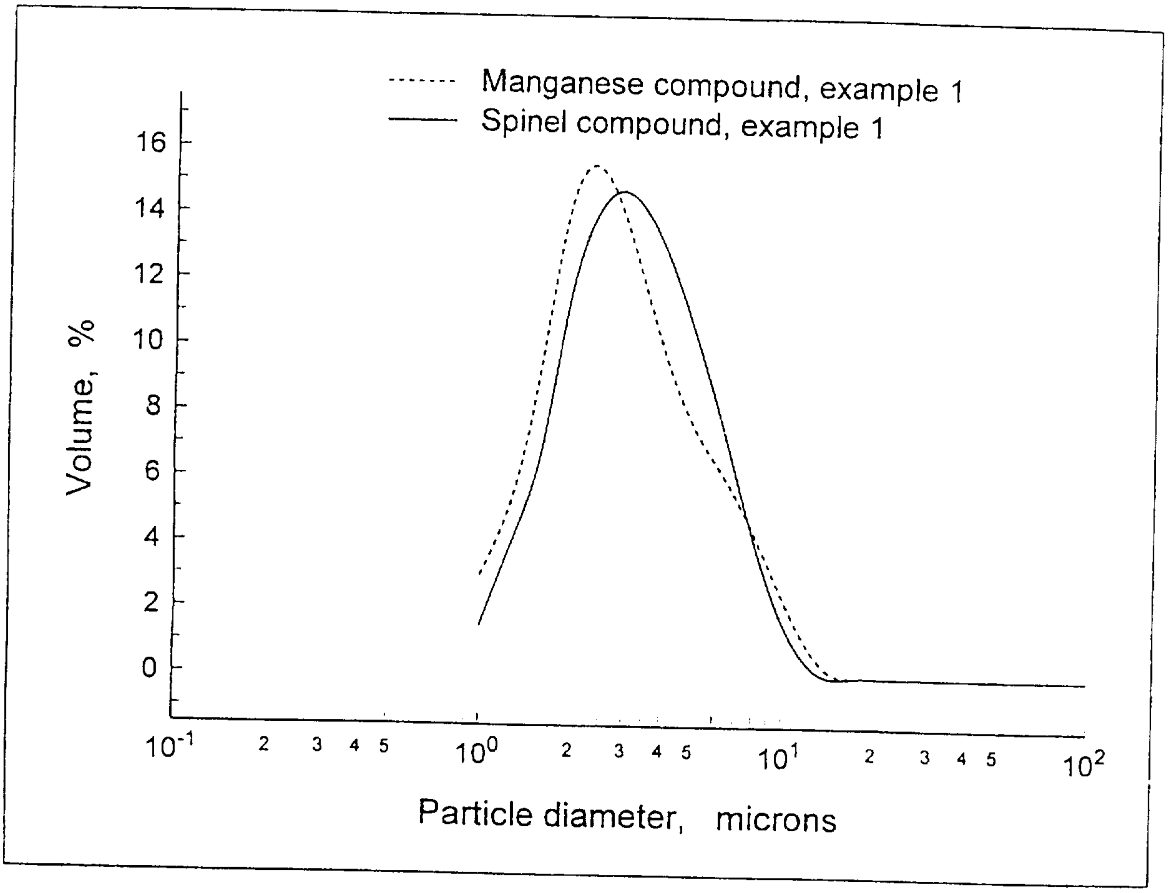
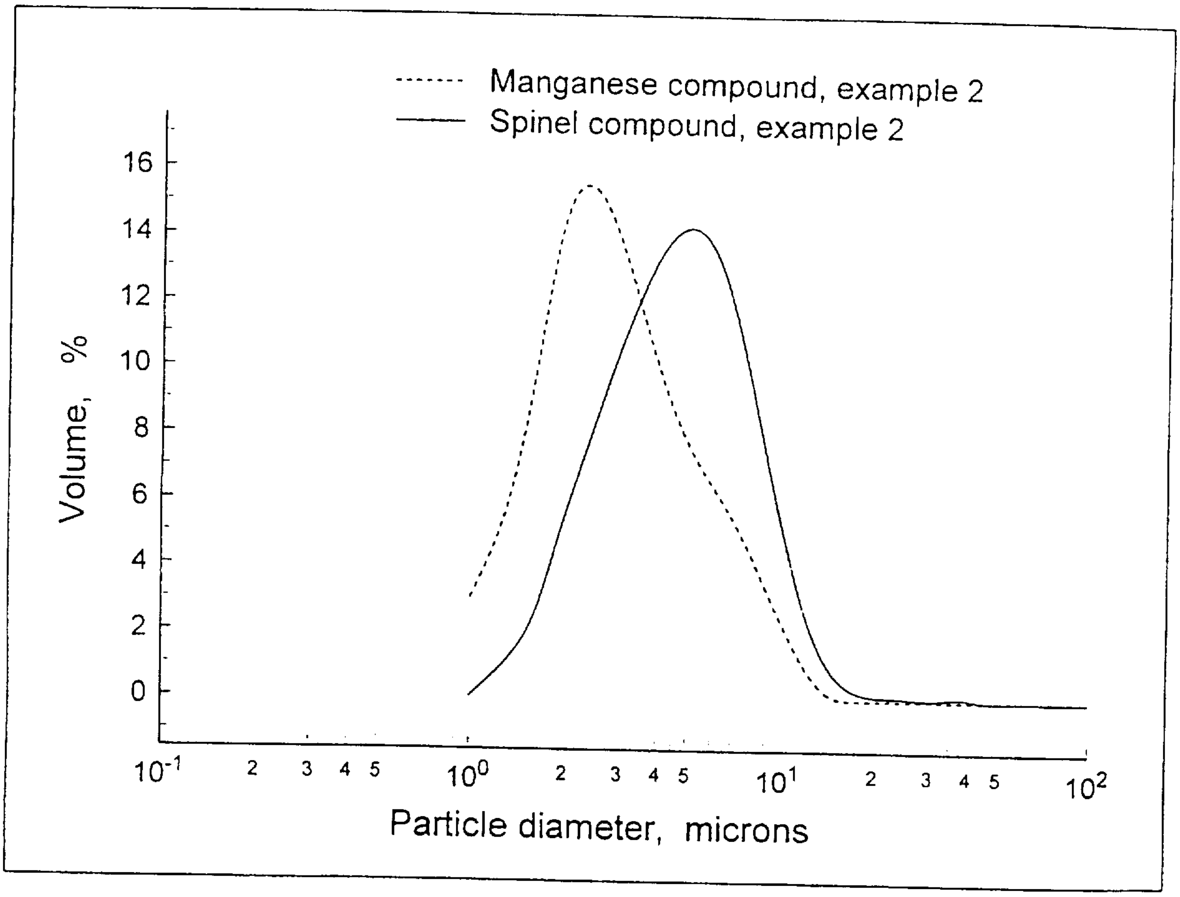

Manganese compound, example 1
Spinel compound, example 1
Volume, %
16
14
12
10
8
6
4
2
0
10^{-1}
2
3
4
5
10^{0}
2
3
4
5
10^{1}
2
3
4
5
10^{2}
Particle diameter, microns

FIG. 1



Manganese compound, example 2
Spinel compound, example 2
Volume, %
16
14
12
10
8
6
4
2
0
10-1
2
3
4
5
10^0
10^1
10^2
Particle diameter, microns

FIG. 2

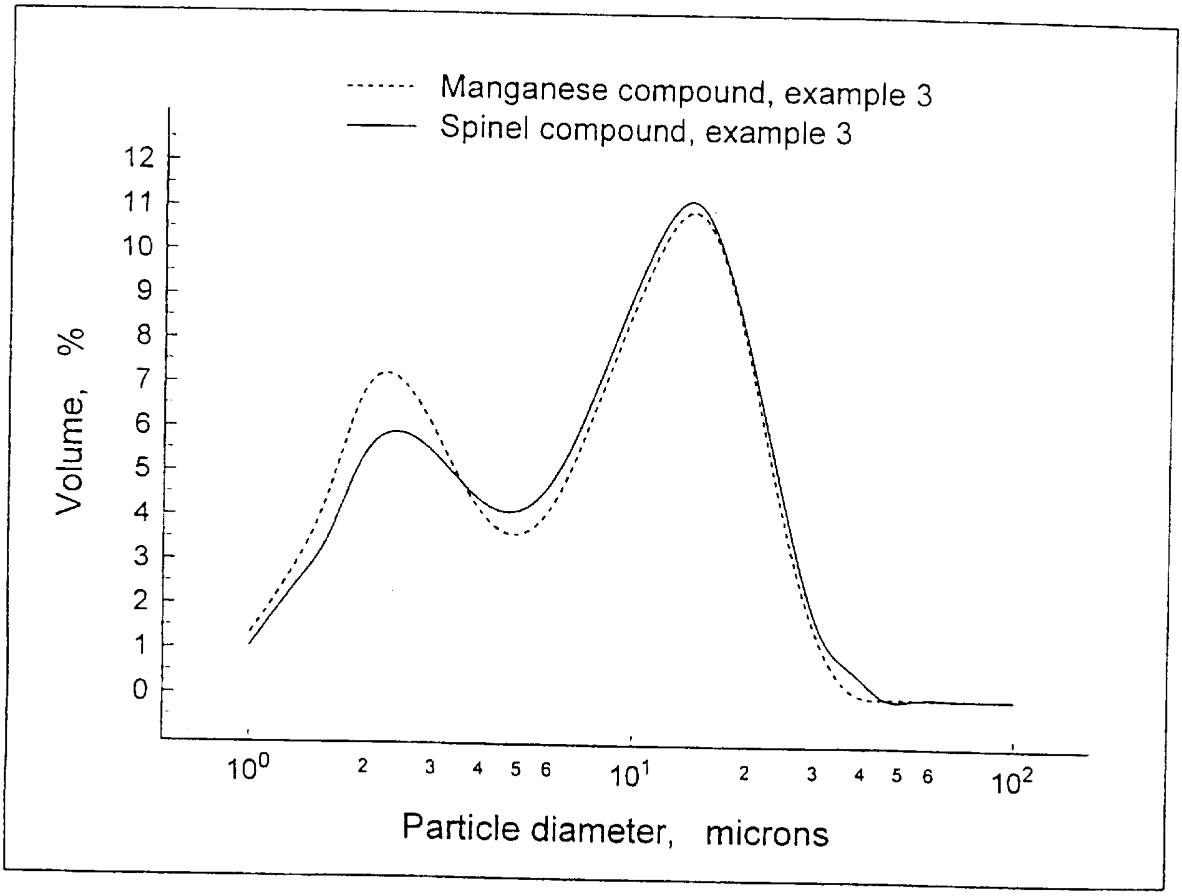

Manganese compound, example 3
Spinel compound, example 3
Volume, %
12
11
10
9
8
7
6
5
4
3
2
1
0
10^0
2
3
4
5
6
10^1
2
3
4
5
6
10^2
Particle diameter, microns

FIG. 3

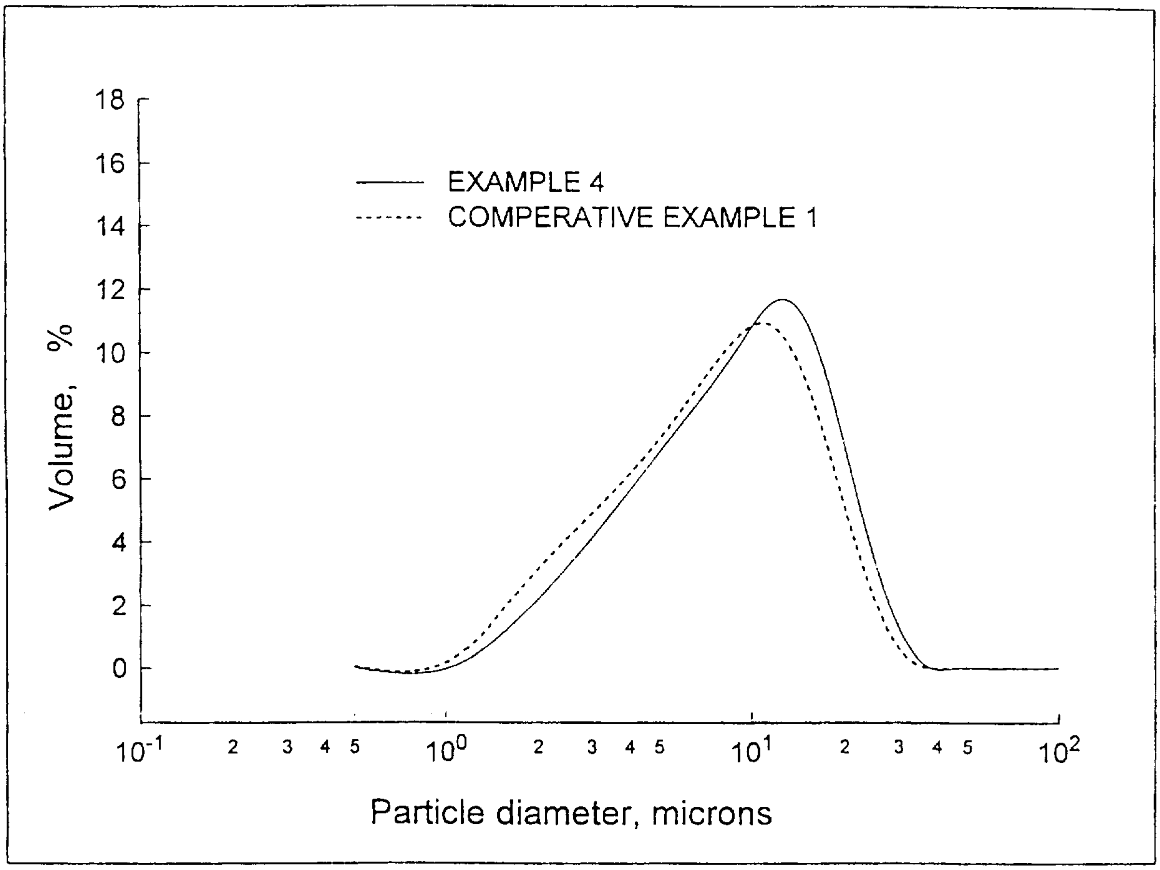

18
16
14
12
10
8
6
4
2
0
Volume, %
EXAMPLE 4
COMPERATIVE EXAMPLE 1
10-1
2
3
4
5
100
2
3
4
5
101
2
3
4
5
102
Particle diameter, microns

FIG. 4

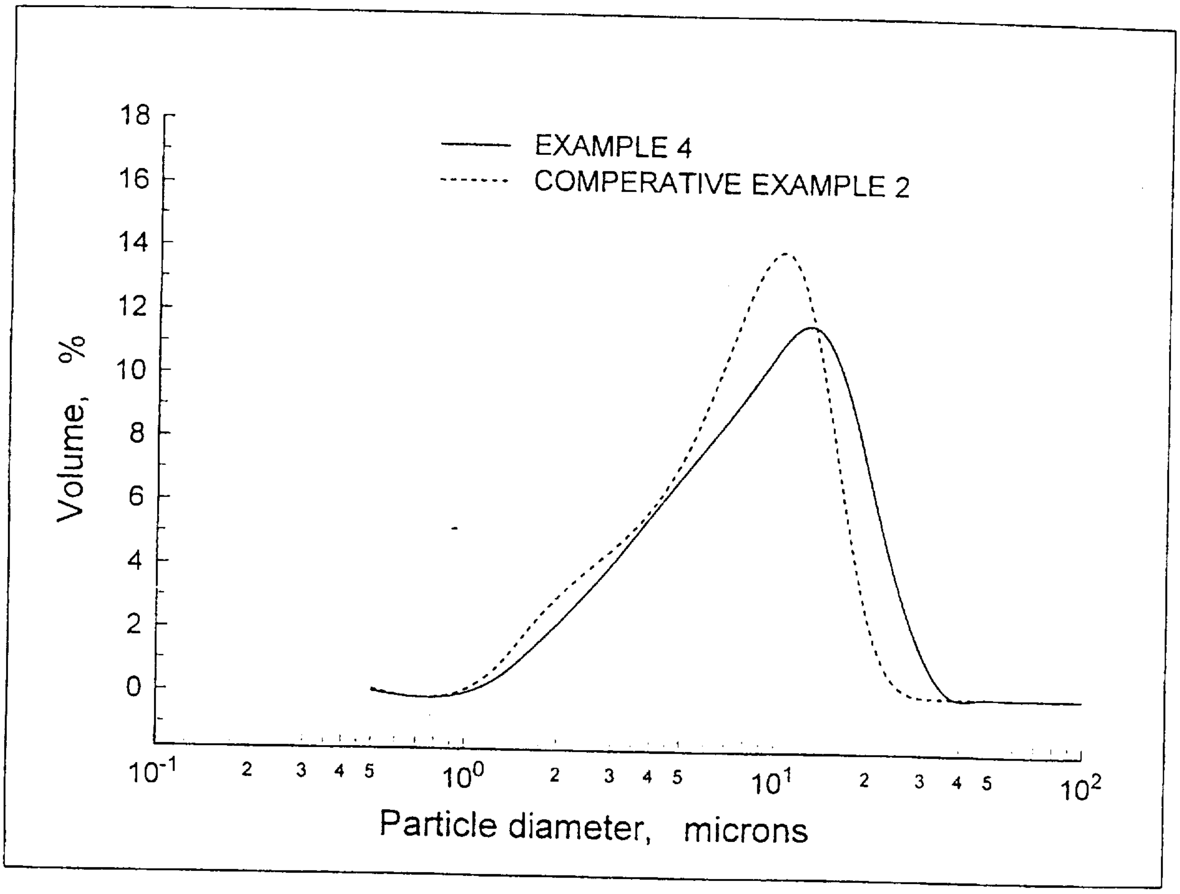

18
16
14
12
10
8
6
4
2
0
Volume, %
EXAMPLE 4
COMPERATIVE EXAMPLE 2
10-1
2
3
4
5
100
2
3
4
5
101
2
3
4
5
102
Particle diameter, microns

FIG. 5

INTERNATIONAL SEARCH REPORT

Interr ıal Application No
PCT/US 97/05550

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	JOURNAL OF POWER SOURCES, vol. 58, no. 2, February 1996, pages 135-138, XP000631998 PISTOIA G ET AL: "SYNTHESIS OF AN EFFICIENT LIMN2O4 FOR LITHIUM-ION CELLS" see the whole document ---	1-5,10, 12,13
A	EP 0 688 739 A (COMMISSARIAT ENERGIE ATOMIQUE ;ELECTRICITE DE FRANCE (FR); BOLLORE) 27 December 1995 ---	
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] 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

1

Date of the actual completion of the international search	Date of mailing of the international search report
26 August 1997	05.09.97

Name and mailing address of the ISA	Authorized officer
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	Brebion, J

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 97/05550

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 140, no. 11, 1 November 1993, pages 3071-3081, XP000424480 GUYOMARD D ET AL: "RECHARGEABLE LI1+XMN2O4/CARBON CELLS WITH A NEW ELECTROLYTE COMPOSITION POTENTIOSTATIC STUDIES AND APPLICATION TO PRACTICAL CELLS" see page 3071 : "Experimental": paragraphs 1 and 2 * ---	2,18,19
A	JOURNAL OF POWER SOURCES, vol. 58, no. 2, February 1996, pages 145-151, XP000632000 SAIDI M Y ET AL: "A MODEL LITHIUM-ION SYSTEM BASED ON THE INSERTION PROPERTIES OF THE SPINEL PHASE LIXMN2O4, (0<X<2)" see page 145, right-hand column, last two lines - page 146, left-hand column, line 1* ---	18
A	JOURNAL OF POWER SOURCES, vol. 54, no. 2, 1 April 1995, pages 323-328, XP000542238 MANEV V ET AL: "RECHARGEABLE LITHIUM BATTERY WITH SPINEL-RELATED λ-MNO2 III.SCALING-UP PROBLEMS ASSOCIATED WITH LIMN2O4 SYNTHESIS" cited in the application ---	
P,A	WO 96 12676 A (VALENCE TECHNOLOGY INC ;PISTOIA GIANFRANCO (IT)) 2 May 1996 see page 17 -----	1-5,10, 12,13,16

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern[illegible]l Application No
PCT/US 97/05550

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0688739 A	27-12-95	FR 2721308 A	22-12-95
		CA 2152226 A	22-12-95
		JP 8203521 A	09-08-96
WO 9612676 A	02-05-96	AU 3893795 A	15-05-96