

TITLEMETHOD FOR PRODUCING LITHIUM MANGANESE OXIDE
INTERCALATION COMPOUNDS AND COMPOUNDS PRODUCED
THEREBY5 FIELD OF THE INVENTION

The invention generally relates to a process for producing lithium manganese oxide intercalation compounds and the compounds so produced, which are particularly well-suited to application as electrodes in lithium batteries.

BACKGROUND OF THE INVENTION

10 Lithium manganese oxide intercalation compounds have long been known in the art. Spinel LiMn_2O_4 was first identified in D. Wickham and W. Croft, J. Phys. Chem Solids, 7, 351 (1958). One method known in the art for producing LiMn_2O_4 involves the solid state reaction of a lithium salt such as Li_2CO_3 with MnO_2 at temperatures in the range of 700-1100°C. In a typical process for
15 producing LiMn_2O_4 , MnO_2 is combined with Li_2CO_3 and reacted at temperatures above 700°C for a period of several hours followed by cooling. A typical reaction process is described by J. C. Hunter in U.S. Patent 4,246,253. The products of such processes can have a wide range of particle sizes dependent on the nature of the starting materials, and reaction temperature and time. Products can also have
20 surface areas ranging from less than 1 m^2/g to greater than 5 m^2/g .

As discussed by Amatucci, et al., J. Power Sources, 69, 11-25 (1997), and by Zhong, et al., U.S. Patent 5,700,597 (1997), use of low surface area LiMn_2O_4 as a cathode can be very important in minimizing the rate of self discharge in electrochemical cells by lowering the rates of electrolyte oxidation and manganese
25 dissolution.

Zhong et al. disclose the use of LiCl at temperatures in the range of 400-750°C to form $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, in the second step of a multi-step heating process, the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ exhibiting unexpected cycling advantages in lithium battery applications.

30 Amatucci et al. disclose spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ wherein $0 < x < 1$, particularly $x=0.05$, having a surface area of about 1 m^2/g or less. The material of Amatucci et al. provides superior performance in lithium battery applications. The desired surface area is achieved by a sequence of anneals at 800°C, intermittent grindings at room temperature, and a final slow cooling.

35 Alternatively, Tarascon, WO 94/26666, discloses a lengthy procedure involving heating at 800°C for about 72 hours, cooling to ambient temperature, grinding, and reheating to 800°C. This process is once again repeated to ensure complete reaction of the starting materials.



Oi et al., Japanese Kokai Patent No. Hei 9(1997)-110431, discloses a method for producing a different lithium manganese oxide, LiMnO_2 , wherein a lithium compound such as lithium carbonate or oxide is combined with a manganese compound such as manganese carbonate or manganese oxy-hydroxide, the lithium to manganese ratio being in the range of 1:0.2 to 1:5, in the presence of a so-called flux of lithium sulfate, lithium borate, or a mixture thereof, the flux being present in the ratio of 0.25 moles or more per mole of manganese. Heating to 800°C - 1100°C for several hours results in the desired product. Oi clearly teaches that in the absence of the flux the spinel LiMn_2O_4 is achieved.

Furthermore, a lithium halide flux is not effective for producing LiMnO_2 .

What are needed are compounds and methods for making those compounds that do not have the deficiencies or problems of the prior art. Other objects and advantages of the present invention will become apparent to those skilled in the art upon reference to the attached drawings and to the detailed description of the invention which hereinafter follows.

SUMMARY OF THE INVENTION

The present invention provides for a composition comprising crystallites of spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, wherein $-0.5 < x < 0.2$, the crystallites being characterized as well-shaped octahedra with average maximum crystalline dimension of greater than 2 micrometers, the crystallites being formed into agglomerates having a surface area of less than $1 \text{ m}^2/\text{g}$.

The present invention further provides for a process for producing spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, the process comprising

Combining a lithium compound (I) with a manganese compound (II), the mole ratio of Li from (I) to Mn from (II) being in the range of about 9:20 to about 12:20, and a third compound (III), selected from the group consisting of alkali or alkaline earth halides, sulfates, borates, and mixtures thereof, whereby the ratio of the sum of the moles of lithium from (I) and the moles of manganese from (II) to the moles of (III) is in the range of about 1:1 to about 100:1, to form a reaction mixture;

Heating the reaction mixture to a temperature in the range of 500 - 1000°C ;

Holding the heated reaction mixture at a temperature in the range of 500 - 1000°C until the desired composition and morphology are achieved;

Cooling the heated reaction mixture at a rate no greater than $60^\circ\text{C}/\text{hr}$ to a temperature less than about 500°C , followed by cooling to room temperature.

The present invention also provides for a process for producing spinel crystallites of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, the process comprising:

- 5 Combining a lithium compound (I) with a manganese compound (II) the mole ratio of Li from (I) to Mn from (II) being in the range of about 9:20 to about 12:20, and a third compound (III) comprising LiCl , whereby the ratio of the sum of the moles of lithium from (I) and the moles of manganese from (II) to the moles of LiCl is in the range of about 1:1 to about 100:1, to form a reaction mixture;
- Heating the reaction mixture to a temperature in the range of 800-900°C;
- 10 Holding the heated reaction mixture at a temperature in the range of 800-900°C until the desired composition and morphology are achieved;
- Cooling the heated reaction mixture at a rate no greater than 60°C/hr to a temperature less than about 500°C, followed by cooling to room temperature.

Further provided in the invention is an electrode comprising the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ of the invention.

BRIEF DESCRIPTION OF THE FIGURES

Figures 1 and 2 are photographs illustrating the difference in crystallite size between the prior art and that of the instant invention, respectively. The product of the process of Tarascon consists of crystallites smaller than 1 micrometer in size, shown in Figure 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides for a novel form of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, and a novel process for synthesizing $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ in less time than required in the processes of the prior art. The product of the present invention is a lithium intercalation compound wherein the Li:Mn ratio suitable for the invention is in the range of 0.9:2 to 1.2:2, with 1.05:2 being preferred. A value of $x < 0.2$ represents a practical limit on the lithium concentration because at values of x greater than about 0.2 the spinel phase desired for the practice of the present invention begins to transform to Li_2MnO_3 .

It will be understood by one of ordinary skill in the art that the formula designation $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ represents an approximation to the actual physical structure of the associated lithium intercalation compound. As pointed out by Amatucci et al., op. cit., the actual empirical formula and Mn:O ratio is likely to vary slightly depending upon the value of x and the manner in which the material is formed. The formula employed herein is consistent with common usage in the art.

The $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ of the invention occurs as agglomerated crystallites, the agglomerates forming particles characterized as having surface areas in the range of 0.1-1 m^2/g as determined by the BET method using nitrogen absorption. When LiCl is employed as at least one component of compound (III) in the process hereinbelow described at a concentration of at least 2% LiCl on the weight of the total composition, the crystallites so formed are characterized by their octahedral habit and average maximum crystalline dimension of greater than 2 micrometers. (see Fig. 2)

The size of the crystallites of the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ of the invention is entirely without precedent in the prior art. Although not bound by this theory, it is believed by the inventors that the unusually large crystallites of the invention are a result of the previously unknown process of the invention hereinbelow described. In particular, it is believed that compound (III) in the process of the invention acts to greatly accelerate the effects of annealing. Long annealing times are required for the formation of large particles of high purity in the processes of Amatucci

04-09-2000

US 009917759

et al. or Tarascon, op cit. Further, it is known from Zhong et al. that synthesis of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ with values of x greater than about 0.05 effectively precludes exposure temperatures in excess of 800°C because of the undesired formation of

Li_2MnO_3 at those temperatures. In the process of the present invention, however, temperatures of about 900°C can be employed which further accelerates annealing, and concomitantly results in a higher purity product in less time, all with negligible formation of Li_2MnO_3 because the duration of exposure to high temperature is so much shorter than in Amatucci et al. or Tarascon.

In the process of the invention, a lithium compound (I) is combined with a manganese compound (II), the mole ratio of Li from (I) to Mn from (II) being in the range of about 9:20 to about 12:20, and a third compound (III) whereby the ratio of the sum of the moles of lithium from (I) and the moles of manganese from (II) to the moles of (III) is in the range of about 1:1 to about 100:1, to form a reaction mixture.

Compound (I) is selected from the group consisting of lithium salts of organic and inorganic acids and oxyacids, and mixtures thereof; preferably lithium halides, acetates, carbonates, oxyhalides, amides, hydroxide, azide, borate, carbide, and hydride, and mixtures thereof; most preferably Li_2CO_3 , LiNO_3 , and LiOH , and mixtures thereof.

Compound (II) is selected from the group consisting of manganese salts of organic and inorganic acids and oxyacids, and oxides, and mixtures thereof; preferably manganese oxides, carbonates, halides, hydroxides, sulfates, acetates, nitrates, sulfides and phosphates; most preferably, MnO_2 , MnCO_3 , and Mn_2O_3 , and mixtures thereof.

Compound (III) is selected from the group consisting of alkali or alkaline earth halides, sulfates, borates, and mixtures thereof. Preferably, compound (III) is selected from the group of alkali metal halides and sulfates, most preferably compound (III) is LiCl or a mixture of LiCl and Li_2SO_4 . Lithium salts are preferred for Compound (III) when the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ formed in the reaction is intended for use in lithium batteries.

The reaction mixture is heated in air to a temperature in the range of $500\text{-}1000^\circ\text{C}$ and held for a period sufficient for the formation of the spinel product of the desired stoichiometry and surface area. While the optimum heating cycle may vary with choice of reactants, stoichiometry, and compound (III), it has been found generally in the process of the invention that processing temperature in the range of $500\text{-}700^\circ\text{C}$ results in higher surface area than does processing in the range of $800\text{-}1000^\circ\text{C}$ other things being equal. In general, reaction times range from about 2 hours to about 16 hours. Although shorter reaction times are feasible at the lower reaction temperatures in order to form the higher surface area products, it is not necessary that the times be held that short. The formation of impurities by competing reactions is more aggravated at higher temperature than at lower temperature.

It has been found in the practice of the invention when temperatures are in the range of 700-1000°C, the particular benefits of the process of the invention are observed most markedly in batches of about 2 kg or larger. In the embodiments of the process of the invention wherein temperatures are in the range of 500-700°C, the benefits of the process are realized even in gram scale reaction mixtures.

In the preferred process of the invention, the reaction mixture is heated in air to a temperature of about 850°C and held for about 8 hours, then heated to 900°C and held an additional about 8 hours followed by cooling to 500°C at a rate of no more than about 60°C/hr, followed, in turn, by cooling to about room temperature. Preferably, the rate of cooling is about 10°C/hr. or less.

The cooled product may then be washed primarily to remove residual compound (III). However, in the most preferred embodiment of the invention, wherein about 2% by weight of LiCl is employed as compound (III), it is believed that some or all of the lithium moiety of compound(III) is incorporated into the product while the associated chlorine moiety is vaporized thus leaving negligible residue and obviating the need for washing. More generally, the alkali metal-containing compounds (III) are preferred over the alkaline earth metal-containing components (III), particularly at the higher compound (III) levels suitable for the practice of the invention, because of the higher solubility in water of the former with respect to the latter.

It has been observed in the practice of the invention that the employment of compound (III) results in a cleaner (i.e., more fully reacted) product at a lower temperature than can be achieved with a given composition at the same temperature absent compound (III). This is even true for the smallest concentration of compound (III) suitable for the practice of the invention. That is to say, the processes of the prior art, all of which omit compound (III), always require a higher temperature and/or greater time to achieve the same result as the process of the present invention.

Purity of the product is thought to influence the performance of the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ of the invention in electrochemical applications where excess "dead" weight is undesirable, and unwanted side reactions of contaminants can degrade performance. The process of the present invention is highly effective at producing a single phase product under highly favorable conditions compared to the prior art, either in shorter cycles or at lower temperatures, or both. Purity is normally determined by x-ray powder diffraction, using techniques well-known in the art. The products of the process of the present invention exhibit only the characteristic x-ray powder diffraction pattern of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$.

The $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ product of the process of the invention occurs as agglomerated crystallites the agglomerates forming particles characterized as

having surface areas in the range of 0.1-20 m²/g. It is found in the practice of the invention that under fixed conditions of thermal exposure and mole ratios, the surface area can be made to vary by an order of magnitude depending upon the alkali metal cation employed in compound (III), higher surface area being
5 associated with higher atomic number of the alkali metal. It is further found in the practice of the invention that, other things being equal, particles of Li_{1+x}Mn₂O₄ produced at reaction temperatures of 500-600°C may have a surface area nearly ten times greater than that of particles produced at 800-900°C depending on the nature of the starting manganese compound. The choice of compound (III) (i.e.,
10 Li, Na, or K containing compounds) affects the surface area in a more general manner.

In a preferred embodiment of the process of the present invention 1 part by mole of Li₂CO₃ is combined with about 3.8 parts of MnO₂ and about 0.1 to about 2 parts, most preferably about 0.1 to about 0.2 parts of Li in the form of LiCl. It
15 has been found that at least some of the LiCl is consumed in the reaction, possibly altering the stoichiometry.

It has further been found in the practice of the invention, that at reaction temperatures in the range of 500-600°C it is preferred to employ the eutectic mixture of LiCl and Li₂SO₄ in place of the LiCl because the eutectic mixture is
20 molten in that temperature range and LiCl is not.

It is further observed in the process of the invention that the process of the invention using LiCl-containing compound (III) at reaction temperature of 800-1000°C, where LiCl is present in levels of about 2% by weight or greater, results in larger crystallites than those obtained by the processes of the prior art.
25

In a surprising aspect of the present invention, it has been found that incorporation of as little as 2 weight % of LiCl or the eutectic mixture of LiCl and Li₂SO₄ in the reaction mixture permits the synthesis of a product of equivalent composition and surface area to that of Amatucci et al., op cit, having distinctive crystallites in a much simpler thermal treatment cycle. A preferred thermal
30 treatment cycle of the invention comprises the following steps:

- a) Heating to about 850°C at a rate of about 4.5°/min and holding for 8 hours
- b) Heating to 900°C at a rate of about 1.5°/min and holding for 8 hours
- 35 c) Cooling at a rate of about 0.1-1°/min to 500°C
- d) Allowing to cool to room temperature.

The resultant product is characterized by a surface area <1 m²/g, and x = about 0.05. When LiCl is present at levels of 2% by weight or greater the resulting product is further characterized as agglomerated crystallites, the

crystallites being well-defined octahedra having an average maximum crystalline dimension of greater than 2 micrometers.

It has been found in the practice of the invention that the choice of compound (III) has a very large effect on the surface area of the resulting product.

5 This is shown in particular hereinbelow in Examples 10 and 11. As presently contemplated, LiCl is preferred. More generally, it should be borne in mind by the practitioner of the instant invention that individual compound (III) exerts a particular influence on surface area and crystallite size, and that when compound (III) is combined, the results may not be predictable.

10 The product produced in the process of the invention is particularly suitable for use as an electroactive material in the cathode of a lithium or lithium ion battery. For such applications, preferably x is about 0.05, and the surface area of the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ less than $1.0 \text{ m}^2/\text{g}$, most preferably about $0.7 \text{ m}^2/\text{g}$. In a preferred manner found suitable for the practice of the invention, a composition is
15 formed comprising $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, and a binder, the composition formed into a shaped article, preferably a film or sheet, most preferably a sheet having a thickness of 250 micrometers or less, the shaped article being useful as a cathode in an electrochemical cell.

Suitable binders include EPDM rubber, polyvinylidene fluoride, and
20 copolymers thereof, polytetrafluoroethylene and copolymers thereof the binders being present at up to 50% by weight, preferably up to 20%. Preferably, the composition contains about 5% of a conductive carbon black. An electrode further comprises an electrolyte.

EXAMPLES

25 The invention is further illustrated by the following non-limiting examples set forth hereinbelow.

EXAMPLE 1 AND COMPARATIVE EXAMPLE 1

To form the reaction mixture of Example 1, 6.4289 g Li_2CO_3 , 40.0000 g MnCO_3 , 8.13 g LiCl, and 3.48 g Li_2SO_4 , were ground together in a mortar and the
30 resultant mixture placed in an uncovered low-form alumina crucible. The reaction mixture of Comparative Example 1 was prepared in a manner identical to that of Example 1 except that the LiCl and Li_2SO_4 were omitted. Both mixtures were reacted in a conventional resistively-heated box furnace by heating in air to 600°C over a 2 hour period, holding at this temperature for 4 hours, followed by slowly
35 cooling at a rate of $1^\circ/\text{min}$ to 500°C , and finally allowing the furnace to cool to room temperature. The reaction product of Example 1 was washed with water and dried under a heat lamp. The surface area thereof, measured by nitrogen BET, was $5.7 \text{ m}^2/\text{g}$. An X-ray powder diffraction (XPD) pattern of this material confirmed that it was clean by showing only the lines of the cubic spinel LiMn_2O_4

structure (International Centre for Diffraction Data, JCPDS-ICCD No. 35-782). On the other hand, the reaction product of Comparative Example 1 showed the presence of Mn_2O_3 and Li_2MnO_3 in addition to the LiMn_2O_4 .

EXAMPLE 2 AND COMPARATIVE EXAMPLE 2

5 The following examples illustrate how the presence of a compound (III) decreases the reaction time and yields a single component product.

To form the reaction mixture of Example 2, 6.3750 g Li_2CO_3 , 30.0000 g MnO_2 , 6.36 g LiCl , and 2.73 g Li_2SO_4 were ground together in a mortar, and placed in an uncovered alumina low-form crucible. The reaction mixture of
10 Comparative Example 2 was prepared in a manner identical to that of Example 2 except that the LiCl and Li_2SO_4 were omitted. Both mixtures were reacted as in Example 1. The reaction product of Example 2 was washed and dried as in Example 1. The surface area thereof, measured by nitrogen BET, was $1.5 \text{ m}^2/\text{g}$. An X-ray powder diffraction pattern of this material confirmed that it was clean
15 by showing only the lines of the cubic spinel LiMn_2O_4 structure (International Centre for Diffraction Data, JCPDS-ICCD No. 35-782). On the other hand, the reaction product of Comparative Example 2 showed the presence of Mn_2O_3 and Li_2MnO_3 in addition to the LiMn_2O_4 .

EXAMPLE 3

20 A second portion of the reaction mixture of Example 2 was processed in the manner of Example 2, except that the reaction was held at 600°C for only 30 minutes. The surface area was $1.5 \text{ m}^2/\text{g}$, and the X-ray powder diffraction pattern of this product was clean, with the pattern showing only the lines of the cubic spinel LiMn_2O_4 structure.

EXAMPLES 4 AND 5

25 After the surprising results observed from the reactions in Examples 1, 2, and 3, the reaction temperature was lowered to 500°C with an essentially identical outcome.

To form the reaction mixture of Example 4, 6.4289 g Li_2CO_3 , 40.0000 g
30 MnCO_3 , 8.13 g LiCl , and 3.48 g Li_2SO_4 were ground together in a mortar, and placed in an uncovered alumina low-form crucible. To form the reaction mixture of Example 5, 6.3750 g Li_2CO_3 , 30.0000 g MnO_2 , 6.36 g LiCl , and 2.73 g Li_2SO_4 were ground together in a mortar, and placed in an uncovered alumina low-form crucible. They were heated in air to 500°C over a 2 hour period, held at 500°C for
35 4 hours, then the furnace was allowed to cool naturally to room temperature. The reaction products were washed with water and dried under a heat lamp. The surface areas, measured by nitrogen BET, were 6.8 and $0.8 \text{ m}^2/\text{g}$ for the MnCO_3 and MnO_2 reactions, respectively. The X-ray powder diffraction patterns of both

products showed no impurity substances, and only the lines of the cubic spinel LiMn_2O_4 structure were present.

EXAMPLES 6-8 AND COMPARATIVE EXAMPLE 3

The benefit of using even low compound (III) levels (2% by weight), as well as the higher level (25% by weight) used in Examples 1-5, is discussed next. It is also demonstrated that these compounds (III) are beneficial on a larger production scale.

The compositions formed in Examples 6-8 and Comparative Example 3 are shown in Table 1 below.

10

TABLE 1

	Example 6	Example 7	Example 8	Comparative Example 3
Li_2CO_3 (kg)	0.280	0.378	0.378	0.378
MnO_2 (kg)	1.300	1.640	1.640	1.640
LiCl (kg)	0.277	0.040	0.016	—
Li_2SO_4 (kg)	0.119	—	0.024	—
Surface Area (m^2/g)	0.5	0.4	0.3	0.3
final product	$\text{Li}_{1.06}\text{Mn}_2\text{O}_4$	$\text{Li}_{1.10}\text{Mn}_2\text{O}_4$	$\text{Li}_{1.07}\text{Mn}_2\text{O}_4$ + trace Li_2SO_4	$\text{Li}_{1.03}\text{Mn}_2\text{O}_4$ Li_2MnO_3

The compositions were mixed by shaking in polyethylene containers for 30 minutes, and each mixture was transferred to an uncovered alumina crucible. The mixtures were processed in air as follows: heated to 850°C over a 3 hour period, held at 850°C for 8 hours, heated to 900°C over a 30 minute period, held at 900°C for 8 hours, and slowly cooled at a rate of $1^\circ/\text{min}$ to 500°C . At this point, the power was turned off, and the furnace cooled naturally to room temperature. In each case, the product formed after reaction was $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ as shown in Table 1.

The reaction product of Example 6 only was washed with water and dried. The products of Examples 6-8 were shown by XPD analyses to be free of impurities, except for the presence of Li_2SO_4 in Example 8 because it had not been washed out. In contrast, the reaction product of Comparative Example 3 was shown by XPD to contain Li_2MnO_3 in addition to the desired material. The surface areas of the reaction products are also shown in Table 1.

EXAMPLE 9 AND COMPARATIVE EXAMPLE 4

This example illustrates the benefit of employing a compound (III) with different starting materials, LiNO_3 and MnCO_3 .

To form the reaction mixture of Example 9, 4.4000 g LiNO_3 , 15.0000 g MnCO_3 , 3.4 g LiCl , and 1.45 g Li_2SO_4 were combined and shaken in a glass jar and placed in an uncovered circular alumina dish. The reaction mixture of Comparative Example 4 was prepared in a manner identical to that of Example 9 except that the LiCl and Li_2SO_4 were omitted. Both reactions were performed by heating in air to 600°C over a 2 hour period, holding at this temperature for 4 hours, and finally allowing the furnace to cool to room temperature. The reaction product of Example 9 was washed with water and dried under a heat lamp. The surface areas for the reaction products of Example 9 and Comparative Example 4, measured by nitrogen BET, were 9.0 and $11.4 \text{ m}^2/\text{g}$, respectively. The X-ray powder diffraction pattern of the reaction product of Example 9 confirmed that it was clean by showing only the lines of the cubic spinel $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$ structure. In clear contrast, the product of the no-compound (III) reaction showed the presence of Mn_2O_3 in addition to the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$.

15 EXAMPLES 10 AND 11

This example shows that, in addition to lithium-containing compound (III), other alkali-metal-containing compound (III) easily produce clean $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, but with higher surface areas.

To form the reaction mixture of Example 10, 7.0903 g Li_2CO_3 , 30.0000 g MnO_2 , 5.19 g NaCl , and 4.08 g Na_2SO_4 were combined and shaken in a glass jar.

To form the reaction mixture of Example 11, 7.0903 g Li_2CO_3 , 30.0000 g MnO_2 , 5.19 g KCl , and 4.08 g K_2SO_4 were combined and shaken in a glass jar.

Both reaction mixtures were loaded into uncovered circular alumina dishes and heated in air in a box furnace. The furnace was ramped up to 850°C over a 3 hour period, held at 850°C for 8 hours, ramped up to 900°C over 10 minutes, held at 900°C for 8 hours, slowly cooled to 500°C at a rate of $1^\circ/\text{min}$, and then allowed to cool naturally to room temperature. The reaction products were washed with water and dried under an infrared heat lamp. The surface areas, measured by nitrogen BET, were 3.9 and $5.5 \text{ m}^2/\text{g}$ for the reaction products of Examples 10 and 11, respectively. X-ray powder diffraction patterns of both products showed that no impurities were present, with only the lines of the cubic spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ structure observed.

30 EXAMPLES 12 AND 13

This example shows that $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ derived from high and low levels of compound (III), i.e., 25% and 2% by weight, have good electrochemical performance as cathodes in rechargeable lithium cells.

In Example 12, 4.00 g of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, synthesized as in Example 7, was combined with 0.215 g of Super P carbon black commercially available from MMM S.A. Carbon, Brussels, Belgium, and 2.5 ml of a 4 wt % solution of EPDM

rubber in cyclohexane. Extra cyclohexane was added to improve flow. The mixture was shaken in a capped glass vial for 15 min. on a mechanical shaker. The resultant slurry was cast onto a sheet of Teflon® FEP and drawn down to form a film using a doctor blade having a 10 mil gap. The dried film was hot-pressed in a roller between Kapton® sheets at 2000 psi and 110°C to form a consolidated sheet suitable for use as a cathode in a lithium battery. The thickness of the sheet was 115 micrometers.

In Example 13, the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ synthesized as in Example 6 was formed into a cathode sheet 80 micrometers thick in a manner identical to that in Example 12.

The resultant consolidated sheets were employed as cathodes against Li metal anodes in electrochemical cells. LiPF_6 in EC/DMC (ethylene carbonate/dimethyl carbonate) served as the electrolyte. Porous polyethylene or glass fiber separators were used between the electrodes. Disks of cathode, anode, and separator were cut with punches. The cathode and separator pieces were soaked in electrolyte solution, then stacked along with the Li into a coin-cell pan and sealed under pressure using the 2325 Coin Cell Crimper System manufactured by the National Research Council Canada.

Both cathodes had good capacity and reversible fraction as shown in Table 2 below.

TABLE 2

Example	x in $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$	Temp(°C)	Capacity (mAh/g)	Reversible Fraction (%)
12	0.06	25	121.4	91.7
13	0.05	25	121.2	92.0

Although particular embodiments of the present invention have been described in the foregoing description, it will be understood by those skilled in the art that the invention is capable of numerous modifications, substitutions and rearrangements without departing from the spirit or essential attributes of the invention. Reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

CLAIMS:

1. A composition comprising crystallites of spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, wherein $-0.5 < x < 0.2$, the crystallites being characterized as well-shaped octahedra with average maximum crystalline dimension of greater than 2 micrometers, the crystallites formed into agglomerates having a surface area of less than $1 \text{ m}^2/\text{g}$.
2. A process for producing spinel crystallites of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, the crystallites being characterized as well-shaped octahedra with average maximum crystalline dimension of greater than 2 micrometers, the crystallites formed into agglomerates having a surface area of less than $1 \text{ m}^2/\text{g}$, the process comprising:
 - Combining a lithium compound (I) with a manganese compound (II) the mole ratio of Li from (I) to Mn from (II) being in the range of about 9:20 to about 12:20, and a third compound (III) comprising LiCl, whereby the ratio of the sum of the moles of lithium from (I) and the moles of manganese from (II) to the moles of LiCl is in the range of about 1:1 to about 100:1, to form a reaction mixture;
 - Heating the reaction mixture to a temperature in the range of $800\text{-}900^\circ\text{C}$;
 - Holding the heated reaction mixture at a temperature in the range of $800\text{-}900^\circ\text{C}$ until the desired composition and morphology are achieved;
 - Cooling the heated reaction mixture at a rate no greater than 60°C/hr to a temperature less than about 500°C , followed by cooling to room temperature.
3. The process of Claim 2 wherein the reaction mixture is heated to about 850°C , followed by holding at about 850°C for about 8 hours, followed by heating to about 900°C followed by holding at about 900°C for about 8 hours.
4. The process of Claim 2 wherein the rate of cooling to 500°C is 10°C/hr or slower.
5. A process for producing spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ the process comprising:
 - Combining a lithium compound (I) with a manganese compound (II), the mole ratio of Li from (I) to Mn from (II) being in the range of about 9:20 to about 12:20, and a third compound (III), selected from the group consisting of alkali or alkaline earth halides, sulfates, borates, and mixtures thereof, whereby the ratio of the sum of the moles of lithium from (I) and the moles of manganese from (II) to the moles of (III) is in the range of about 1:1 to about 100:1, to form a reaction mixture;

Heating the reaction mixture to a temperature in the range of 500-1000°C;

Holding the heated reaction mixture at a temperature in the range of 500-1000°C until the desired composition and morphology are achieved;

Cooling the heated reaction mixture at a rate no greater than 60°C/hr to a temperature less than about 500°C, followed by cooling to room temperature.

6. The process of Claim 5 wherein the reaction mixture is heated to about 850°C, followed by holding at about 850°C for about 8 hours, followed by heating to about 900°C, followed by holding at about 900°C for about 8 hours.

7. The process of Claim 5 wherein the rate of cooling to 500°C is 10°C/hr or slower.

8. The composition of Claim 1 wherein x is about 0.05.

9. The process of Claims 2 or 5 wherein the Li:Mn mole ratio is about 1:1.9.

10. The process of Claims 2 or 5 wherein the lithium compound is selected from the group consisting of lithium salts of organic and inorganic acids and oxyacids, and mixtures thereof.

11. The process of Claims 2 or 5 wherein the lithium compound is selected from the group consisting of lithium halides, acetates, carbonates, oxyhalides, amides, hydroxide, azide, borate, carbide, and hydride, and mixtures thereof.

12. The process of Claims 2 or 5 wherein the lithium compound is selected from the group consisting of Li_2CO_3 , LiNO_3 , and LiOH , and mixtures thereof.

13. The process of Claims 2 or 5 wherein the manganese compound is selected from the group consisting of manganese salts of organic and inorganic acids and oxyacids, and oxides, and mixtures thereof.

14. The process of Claims 2 or 5 wherein the manganese compound is selected from the group consisting of manganese oxides, carbonates, halides, hydroxides, sulfates, acetates, nitrates, sulfides and phosphates, and mixtures thereof.

15. The process of Claims 2 or 5 wherein the manganese compound is selected from the group consisting of MnO_2 , MnCO_3 , and Mn_2O_3 , and mixtures thereof.

16. The process of Claim 5 wherein compound (III) is selected from the group consisting of alkali metal halides and sulfates, and mixtures thereof.

17. The process of Claim 5 wherein compound (III) is LiCl or a mixture of LiCl and Li_2SO_4 .
18. The process of Claims 2 or 5 further comprising the step of washing the reacted product thereof.
- 5 19. An electrode comprising the composition of Claim 1.
20. An electrochemical cell comprising the electrode of Claim 19.
21. The electrode of Claim 19 further comprising a binder.
22. The electrode of Claim 21 further comprising carbon black.
23. A spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ produced by the process of Claims 2 or 5.
- 10 24. An electrode comprising the spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ of Claim 23.