

FP 536 - DE

65779 Kelkheim, 16.08.93

T U 2 - Dr.Ns/th

VARTA Batterie Aktiengesellschaft**Am Leineufer 51, 30419 Hanover****Patent claims**

1. Process for producing a positive electrode for
5 lithium secondary batteries whose active material is
composed of a lithium manganese oxide having a spinel
structure and formed by mixing manganese dioxide with
lithium formate and/or lithium acetate and subsequently
heating the mixture, characterized in that the mixture is
10 heated at a temperature of 550°C to 800°C for between 10
and 100 hours and is then ground.
2. Process according to Claim 1, characterized in
that the mixture is heated at a temperature of 600°C to
750°C.
- 15 3. Process according to Claim 1 or 2, characterized
in that the manganese dioxide is a chemically produced
product (CMD) or a β -MnO₂ (pyrolusite).
4. Process according to one of Claims 1 to 3,
characterized in that the constituents of the mixture
20 contain manganese and lithium in a molar ratio of Mn:Li
= 2:x, where $0.5 < x < 1.5$, preferably $0.9 < x < 1.2$.
5. Process according to one of Claims 1 to 4,
characterized in that the mixture is produced by spray-
drying a suspension of manganese dioxide in an aqueous
25 solution of the appropriate lithium salts.

REPLACED SHEETS		SG
☒	Description : paged2... to paged5.....	
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Process for producing a positive electrode for lithium secondary batteries

The invention relates to a process for producing a positive electrode for lithium secondary batteries whose active material is composed of a lithium manganese oxide having a spinel structure and formed by mixing manganese dioxide with lithium formate and/or lithium acetate and subsequently heating the mixture.

Lithium-manganese spinels are at present used with great advantage as positive electrode material in electrochemical cells of the $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ type. The charge/discharge mechanism of such cells is based on the capacity of the manganese oxide to intercalate and de-intercalate active Li^+ ions reversibly in its spinel lattice, which forms an open skeleton structure. Consequently, x also changes in parallel with progressive charging or discharging.

To prepare an LiMn_2O_4 material from MnO_2 , the starting point is usually a commercially available manganese dioxide which is thoroughly ground in a mortar with a solid lithium compound, for example lithium hydroxide, lithium carbonate or lithium iodide, and is then heated for the purpose of sintering.

The sinter cake may optionally be comminuted and provided with a conductive agent (graphite) and a binder before it is press-moulded to form the finished cathode pellet.

The commercially available manganese oxides (manganese blacks) form a suitable starting material for the preparation of lithium-manganese spinels insofar as they have already been used for a long time in the battery industry, their electrochemical behaviour has been thoroughly researched, they are an inexpensive raw material and they present no problems in relation to environmental compatibility.

The cathode substances produced in the manner described have, however, hitherto continued to suffer from the lack of inadequate cycle stability. The



dischargeable capacities decrease noticeably in the course of the cyclic service life, in particular after a preceding high-temperature ageing.

5 There has therefore been no lack of proposals for stabilizing the host structure of the manganese spinel, for example by substituting some of the manganese in the lattice by foreign metals, including Co, Ni, Fe. Unqualified successes have, however, failed to materialize.

10 It is also known from Japanese Published Specification 4,169065 to produce a positive electrode material for lithium batteries from MnO_2 and lithium salts of formic acid and acetic acid, with which the manganese oxide is mixed instead of $\text{LiOH}\cdot\text{H}_2\text{O}$ or Li_2CO_3 . The mixture is heat-treated at relatively low temperatures of between
15 200°C and 500°C.

The object of the invention is to provide a process for producing a lithium-manganese spinel of the $\text{Li}_x\text{Mn}_2\text{O}_4$ type which is found to be cyclically stable as cathode material in lithium cells containing organic
20 electrolytes and is suitable as counterelectrode to a negative lithium electrode of the intercalation type (Li in a carbon matrix), in particular even in systems in which lithium is intercalated in both electrodes (so-called "SWING" systems).

25 The object is achieved, according to the invention, by a process such as that defined in Patent Claim 1.

According to Claim 1, an intimate mixture of pure manganese oxide and lithium formate, HCOOLi , or lithium
30 acetate, CH_3COOLi , optionally also of both salts, is prepared as a first step.

A preferably useable manganese dioxide is prepared by a chemical reaction, usually by precipitation from manganese salt solutions, and [lacuna] a marketable
35 product as "chemical" manganese dioxide (CMD). Pure $\beta\text{-MnO}_2$, which occurs naturally as pyrolusite, is, however, also suitable as starting material.

The constituents mentioned are mixed in such quantitative proportions that a molar ratio of $\text{Mn}:\text{Li} =$



2:x, where $0.5 < x < 1.5$, preferably $0.9 < x < 1.2$, is produced.

5 A particularly intimate mixing is obtained if a suspension of the manganese black is produced in an aqueous solution of the appropriate lithium salts and said solution is then subjected to spray drying.

10 The mixture obtained (in the latter case, the dry residue obtained) is heated at 550°C to 800°C , preferably at 600°C to 750°C , in air for between 10 and 100 hours. This thermal treatment produces, as a result of the vigorous gas evolution accompanying the reaction of the mixture components, an extremely finely crystalline lithium-manganese spinel. The small particle size of this preparation corresponds to a relatively large BET surface area ($>5\text{m}^2/\text{g}$). This in turn imparts good high-current properties to the manganese spinel produced according to the invention.

The product is then ground and processed to produce the electrode.

20 The active electrode material produced in this way meets the requirement for good cycle stability in batteries having positive LiMn_2O_4 electrodes and negative Li or Li-intercalating electrodes. It is also notable for high-temperature stability and is therefore suitable even for use in galvanic solid-electrolyte cells which are operated in the temperature ranges above room temperature.

30 Finally, the capacity to dope the present lithium-manganese spinels with lithium to far beyond the stoichiometric composition (not more than $x = 1.5$) is found to be extremely advantageous, especially in relation to the production of cells having positive and negative lithium-intercalating electrodes (SWING system).

35 In the finally assembly and sealed state, the electrodes of such cells are usually uncharged, i.e. all the available lithium is incorporated in the positive spinel or metal oxide electrode, while the host structure of the negative electrode is drained of lithium.

During the first charge, lithium is discharged

from the positive host lattice and incorporated into the negative host lattice, preferably a carbon matrix. Some of the lithium is now retained by the carbon matrix to form a covering layer, i.e. by an irreversible chemical reaction, and a certain quantity of lithium is withdrawn in this way from the intercalation mechanism by the carbon material, which is not inert, from the outset.

A lithium-manganese spinel made up with a hyperstoichiometric amount of lithium makes it possible, however, to saturate the reactivity of the carbon electrode, so that the intercalation and deintercalation of the lithium in the carbon matrix can proceed virtually without loss, that is to say reversibly.

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Abstract

Process for producing a positive electrode for lithium secondary batteries

5 A lithium-manganese oxide $\text{Li}_x\text{Mn}_2\text{O}_4$ having a spinel structure is prepared as cathode material for lithium secondary batteries by mixing manganese dioxide with lithium formate and/or lithium acetate (HCOOLi , CH_3OOLi) and subsequently heating the mixture at, preferably, 600°C to 750°C for 10 to 100 hours. The mixture components contain manganese and lithium in a molar ratio of Mn:Li = 2:x, where $0.5 < x < 1.5$. The final product is extremely finely crystalline and is notable for good cycle stability.

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1-4330012

VARTA Batterie Aktiengesellschaft

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Patent claims

1. Process for producing a positive electrode for lithium secondary batteries whose active material is composed of a lithium manganese oxide having a spinel structure and formed by mixing manganese dioxide with lithium formate and/or lithium acetate and subsequently heating the mixture, characterized in that the mixture is heated at a temperature of 550°C to 800°C for between 10 and 100 hours and is then ground.
2. Process according to Claim 1, characterized in that the mixture is heated at a temperature of 600°C to 750°C.
3. Process according to Claim 1 or 2, characterized in that the manganese dioxide is a chemically produced product (CMD) or a β -MnO₂ (pyrolusite).
4. Process according to one of Claims 1 to 3, characterized in that the constituents of the mixture contain manganese and lithium in a molar ratio of Mn:Li = 2:x, where $0.5 < x < 1.5$, preferably $0.9 < x < 1.2$.
5. Process according to one of Claims 1 to 4, characterized in that the mixture is produced by spray-drying a suspension of manganese dioxide in an aqueous solution of the appropriate lithium salts.

REPLACEMENT SHEETS SG

- ☒ Description : paged 2 to paged 5.
☒ Claim(s) : paged 1 to paged 1.
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- ☒ Description : paged 2 to paged 5.
☒ Claim(s) : paged 1 to paged 1.
☐ Drawing(s) : paged to paged
☒ Abstract : paged 4 to paged 4.

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Process for producing a positive electrode for lithium secondary batteries

The invention relates to a process for producing a positive electrode for lithium secondary batteries whose active material is composed of a lithium manganese oxide having a spinel structure and formed by mixing manganese dioxide with lithium formate and/or lithium acetate and subsequently heating the mixture.

Lithium-manganese spinels are at present used with great advantage as positive electrode material in electrochemical cells of the $\text{Li/LiMn}_2\text{O}_4$ type. The charge/discharge mechanism of such cells is based on the capacity of the manganese oxide to intercalate and de-intercalate active Li^+ ions reversibly in its spinel lattice, which forms an open skeleton structure. Consequently, x also changes in parallel with progressive charging or discharging.

To prepare an LiMn_2O_4 material from MnO_2 , the starting point is usually a commercially available manganese dioxide which is thoroughly ground in a mortar with a solid lithium compound, for example lithium hydroxide, lithium carbonate or lithium iodide, and is then heated for the purpose of sintering.

The sinter cake may optionally be comminuted and provided with a conductive agent (graphite) and a binder before it is press-moulded to form the finished cathode pellet.

The commercially available manganese oxides (manganese blacks) form a suitable starting material for the preparation of lithium-manganese spinels insofar as they have already been used for a long time in the battery industry, their electrochemical behaviour has been thoroughly researched, they are an inexpensive raw material and they present no problems in relation to environmental compatibility.

The cathode substances produced in the manner described have, however, hitherto continued to suffer from the lack of inadequate cycle stability. The dischargeable capacities decrease noticeably in the

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course of the cyclic service life, in particular after a preceding high-temperature ageing.

There has therefore been no lack of proposals for stabilizing the host structure of the manganese spinel, for example by substituting some of the manganese in the lattice by foreign metals, including Co, Ni, Fe. Unqualified successes have, however, failed to materialize.

It is also known from Japanese Published Specification 4,169065 to produce a positive electrode material for lithium batteries from MnO_2 and lithium salts of formic acid and acetic acid, with which the manganese oxide is mixed instead of $\text{LiOH} \cdot \text{H}_2\text{O}$ or Li_2CO_3 . The mixture is heat-treated at relatively low temperatures of between 200°C and 500°C .

The object of the invention is to provide a process for producing a lithium-manganese spinel of the $\text{Li}_x\text{Mn}_2\text{O}_4$ type which is found to be cyclically stable as cathode material in lithium cells containing organic electrolytes and is suitable as counterelectrode to a negative lithium electrode of the intercalation type (Li in a carbon matrix), in particular even in systems in which lithium is intercalated in both electrodes (so-called "SWING" systems).

The object is achieved, according to the invention, by a process such as that defined in Patent Claim 1.

According to Claim 1, an intimate mixture of pure manganese oxide and lithium formate, HCOOLi , or lithium acetate, CH_3COOLi , optionally also of both salts, is prepared as a first step.

A preferably useable manganese dioxide is prepared by a chemical reaction, usually by precipitation from manganese salt solutions, and [lacuna] a marketable product as "chemical" manganese dioxide (CMD). Pure $\beta\text{-MnO}_2$, which occurs naturally as pyrolusite, is, however, also suitable as starting material.

The constituents mentioned are mixed in such quantitative proportions that a molar ratio of $\text{Mn}:\text{Li} = 2:x$, where $0.5 < x < 1.5$, preferably $0.9 < x < 1.2$, is

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produced.

A particularly intimate mixing is obtained if a suspension of the manganese black is produced in an aqueous solution of the appropriate lithium salts and said solution is then subjected to spray drying.

The mixture obtained (in the latter case, the dry residue obtained) is heated at 550°C to 800°C, preferably at 600°C to 750°C, in air for between 10 and 100 hours. This thermal treatment produces, as a result of the vigorous gas evolution accompanying the reaction of the mixture components, an extremely finely crystalline lithium-manganese spinel. The small particle size of this preparation corresponds to a relatively large BET surface area ($>5\text{m}^2/\text{g}$). This in turn imparts good high-current properties to the manganese spinel produced according to the invention.

The product is then ground and processed to produce the electrode.

The active electrode material produced in this way meets the requirement for good cycle stability in batteries having positive LiMn_2O_4 electrodes and negative Li or Li-intercalating electrodes. It is also notable for high-temperature stability and is therefore suitable even for use in galvanic solid-electrolyte cells which are operated in the temperature ranges above room temperature.

Finally, the capacity to dope the present lithium-manganese spinels with lithium to far beyond the stoichiometric composition (not more than $x = 1.5$) is found to be extremely advantageous, especially in relation to the production of cells having positive and negative lithium-intercalating electrodes (SWING system).

In the finally assembly and sealed state, the electrodes of such cells are usually uncharged, i.e. all the available lithium is incorporated in the positive spinel or metal oxide electrode, while the host structure of the negative electrode is drained of lithium.

During the first charge, lithium is discharged from the positive host lattice and incorporated into the

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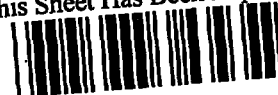
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negative host lattice, preferably a carbon matrix. Some of the lithium is now retained by the carbon matrix to form a covering layer, i.e. by an irreversible chemical reaction, and a certain quantity of lithium is withdrawn in this way from the intercalation mechanism by the carbon material, which is not inert, from the outset.

A lithium-manganese spinel made up with a hyperstoichiometric amount of lithium makes it possible, however, to saturate the reactivity of the carbon electrode, so that the intercalation and deintercalation of the lithium in the carbon matrix can proceed virtually without loss, that is to say reversibly.

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Abstract

Process for producing a positive electrode for lithium secondary batteries

A lithium-manganese oxide $\text{Li}_x\text{Mn}_2\text{O}_4$, having a spinel structure is prepared as cathode material for lithium secondary batteries by mixing manganese dioxide with lithium formate and/or lithium acetate (HCOOLi , CH_3OOLi) and subsequently heating the mixture at, preferably, 600°C to 750°C for 10 to 100 hours. The mixture components contain manganese and lithium in a molar ratio of $\text{Mn}:\text{Li} = 2:x$, where $0.5 < x < 1.5$. The final product is extremely finely crystalline and is notable for good cycle stability.

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The cathode substances prepared in the manner described have, however, suffered hitherto from the defect of unsatisfactory cyclical stability. The dischargeable capacities fall appreciably during the cyclical service life, in particular in the event of

previous storage at high temperature.

There has therefore been no shortage of proposals for stabilising the host structure of the manganese spinel, for example by substituting foreign metals, including Co, Ni, Fe, for some of the manganese in the lattice. Real success has, however, proved elusive.

JP-OS 4-169065 also discloses preparing a positive electrode material for lithium batteries from MnO_2 and lithium salts of formic acid and of acetic acid, with which the manganese oxide is mixed instead of $\text{LiOH} \cdot \text{H}_2\text{O}$ or Li_2CO_3 . The mixture is tempered at relatively low temperatures of between 200 and 500°C.

The object of the invention is to indicate a process for preparing a lithium manganese spinel of the $\text{Li}_x\text{Mn}_2\text{O}_4$ type, which proves to be a cyclically stable cathode material in lithium cells having organic electrolytes and which, in particular in systems in which lithium is intercalated in both electrodes (known as "SWING" systems), is also suitable as the counter-electrode to a negative lithium electrode of the intercalation type (Li in a carbon matrix).

The object is achieved according to the invention by a process as defined in Claim 1.

According to Claim 1, there is prepared in the first step an intimate mixture of pure manganese oxide and lithium formate, HCOOLi , or lithium acetate, CH_3COOLi , also optionally of both salts, with particularly intimate mixing being achieved by preparing in an aqueous solution of the corresponding lithium salts a suspension of manganese dioxide which is then spray-dried.

A manganese dioxide which can be utilised preferably is obtained by chemical reactions, generally by precipitation from manganese salt solutions, and is a product which is currently marketed as

"chemical" manganese dioxide (CMD). However, pure β - MnO_2 , which occurs naturally as pyrolusite, is also a suitable starting material.

The named constituents are mixed in quantities such that there results a molar ratio of Mn : Li of 2 : x where $0.5 < x < 1.5$, preferably $0.9 < x < 1.2$.

The mixture - in the latter case the dry residue - obtained is in a second step heated in air at from 600°C to 750°C for between 10 and 100 hours. Because of the vigorous gas generation accompanying the reaction of the mixture components, this thermal treatment results in an extremely finely crystalline lithium manganese spinel. The small particle size of this preparation corresponds with a relatively large BET surface area ($> 5 \text{ m}^2/\text{g}$). This in turn imparts good high-current properties to the manganese spinel prepared according to the invention.

The product is then ground and processed to form the electrode.

The active electrode material thus prepared satisfies the requirement for good cyclical stability in batteries having positive $\text{Li}_x\text{Mn}_2\text{O}_4$ electrodes and negative lithium or lithium-intercalating electrodes. It is further distinguished by high temperature stability and is therefore also suitable for use in galvanic solid electrolyte cells which are operated within temperature ranges above room temperature.

Finally, a striking advantage, especially with a view to preparing cells having positive and negative lithium-intercalating electrodes (swing system), is the ability of the present lithium manganese spinel to be doped with lithium to an extent far above the stoichiometric composition (maximum $x = 1.5$).

The electrodes of such cells in the ready installed and sealed state are normally uncharged, that is to say all the available

lithium is included in the positive spinel electrode or metal oxide electrode, while the host structure of the negative electrode is emptied of lithium.

On the first charging, there takes place exclusion of the lithium from the positive host lattice and inclusion in the negative host lattice, preferably a carbon matrix. Now some of the lithium is fixed by the carbon matrix with formation of a covering layer, namely as a result of an irreversible chemical reaction, and in this manner a certain quantity of lithium is removed from the intercalation mechanism from the outset as a result of the chemically not indifferent carbon material.

However, a lithium manganese spinel formulated according to the invention with a hyperstoichiometric quantity of lithium makes it possible to satisfy the reactivity of the carbon electrode such that the intercalation and de-intercalation of the lithium in the carbon matrix is able to take place virtually without loss, that is to say reversibly.



Claims

1. Process for preparing a positive electrode for secondary lithium batteries, whereof the active material comprises a lithium manganese oxide having spinel structure, which is formed by spray-drying a suspension of manganese dioxide in an aqueous solution of lithium formate and/or lithium acetate, followed by heating the mixture, with the mixture being heated at a temperature of from 600 to 750°C for between 10 and 100 hours and then ground.
2. Process according to Claim 1, in which the manganese oxide is a chemically generated product (CMD) or a β -MnO₂ (pyrolusite).
3. Process according to one of Claims 1 or 2, in which the constituents of the mixture contain manganese and lithium in a molar ratio of Mn : Li of 2 : x, where $0.5 < x < 1.5$, preferably $0.9 < x < 1.2$.

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Abstract**PROCESS FOR PREPARING A POSITIVE ELECTRODE FOR SECONDARY LITHIUM
BATTERIES**

A lithium-manganese oxide $\text{Li}_x\text{Mn}_2\text{O}_4$, having a spinel structure is prepared as cathode material for lithium secondary batteries by mixing manganese dioxide with lithium formate and/or lithium acetate (HCOOLi , CH_3OOLi) and subsequently heating the mixture at, preferably, 600°C to 750°C for 10 to 100 hours. The mixture components contain manganese and lithium in a molar ratio of $\text{Mn}:\text{Li} = 2:x$, where $0.5 < x < 1.5$. The final product is extremely finely crystalline and is notable for good cycle stability.

