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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.

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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
5 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 $\text{Li/Li}_x\text{Mn}_2\text{O}_4$ 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
10 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
20 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
30 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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