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D E C I S I O N
of 5 February 2003

Case Number: T 0947/01 - 3.4.2
Application Number: 95119801.9
Publication Number: 0720247
IPC: H01M 4/52, C01G 53/00, H01M 4/50

Language of the proceedings: EN

Title of invention:

Manufacturing processes of positive active materials for lithium secondary batteries and lithium secondary batteries comprising the same

Patentee:

MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.

Opponent:

H.C. STARCK GmbH & Co. KG

Headword:

-

Relevant legal provisions:

EPC Art. 56

Keyword:

"Inventive step (confirmed)"

Decisions cited:

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Catchword:

-



Case Number: T 0947/01 - 3.4.2

D E C I S I O N
of the Technical Board of Appeal 3.4.2
of 5 February 2003

Appellant:
(Opponent)

H.C. STARCK GmbH & Co. KG
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Representative:

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Respondent:
(Proprietor of the patent)

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Representative:

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Decision under appeal:

Decision of the Opposition Division of the
European Patent Office posted 25 July 2001
rejecting the opposition filed against European
patent No. 0 720 247 pursuant to Article 102(2)
EPC.

Composition of the Board:

Chairman: E. Turrini
Members: A. G. M. Maaswinkel
V. Di Cerbo

Summary of Facts and Submissions

- I. The appellants (opponents) lodged an appeal, received on 14 August 2001, against the decision of the opposition division, dispatched on 25 July 2001, to reject the opposition against the European patent No. 0 720 247. The fee for the appeal was paid on 14 August 2001. The statement setting out the grounds of appeal was received on 16 October 2001.
- II. Opposition had been filed against the patent as a whole on the basis of Article 100(a) EPC, and in particular on the grounds that the subject-matter of the patent was not patentable within the terms of Articles 52 to 57 EPC because it did not involve an inventive step. To support their objections the opponents referred *inter alia* to the following documents:
- (D1) GB-A-1 306 374
- (D2) US-A-4 567 031
- (D5) EP-A-0 468 942
- (D7) JP-A-1 294 364 and English translation.
- III. On 5 February 2003 oral proceedings were conducted.
- IV. At the oral proceedings the appellants requested that the decision under appeal be set aside and that the patent be revoked.
- V. The respondents requested that the appeal be dismissed and that the patent be maintained as granted.

VI. The wording of independent claim 1 reads as follows:

"A manufacturing process of positive active materials for lithium secondary batteries comprising lithium containing oxides, nickel and cobalt, represented by a formula $\text{LiNi}_x\text{Co}(1-x)\text{O}_2$, where the value x is $0,50 \leq x \leq 0,95$; wherein composite hydroxides comprising cobalt and nickel are provided through coprecipitation of cobalt and nickel hydroxides by adding caustic alkali aqueous solutions to mixed aqueous solutions containing cobalt and nickel salts, which composite hydroxides are then mixed with lithium compounds and burned at a temperature not less than 600°C and not more than 800°C ."

The wording of independent claim 4 reads as follows:

"A manufacturing process of positive active materials for lithium secondary batteries comprising lithium containing oxides, nickel and manganese, represented by a formula $\text{LiNi}_x\text{Mn}(1-x)\text{O}_2$, where the value x is $0,95 \geq x \geq 0,70$; wherein composite hydroxides comprising manganese and nickel are provided through coprecipitation of manganese and nickel hydroxides by adding caustic alkali aqueous solutions to mixed aqueous solutions containing manganese and nickel salts, which composite hydroxides are then mixed with lithium compounds and burned at a temperature not less than 600°C and not more than 800°C ."

The wording of independent claim 7 reads as follows:

"A manufacturing process of lithium secondary batteries; wherein composite hydroxides comprising cobalt and nickel are provided through coprecipitation of cobalt and a nickel hydroxides by adding caustic alkali aqueous solutions to mixed aqueous solutions containing cobalt and nickel salts, which composite

hydroxides are then mixed with lithium compounds and burned at a temperature not less than 600°C and not more than 800°C to make positive active materials represented by a formula $\text{LiNi}_x\text{Co}(1-x)\text{O}_2$, where the value x is $0,50 \leq x \leq 0,95$; and paste containing the said positive active materials are coated on aluminium foils constituting the positive electrodes of the batteries."

The wording of independent claim 8 reads as follows:

"A manufacturing process of lithium secondary batteries; wherein composite hydroxides comprising manganese and nickel are provided through coprecipitation of manganese and nickel hydroxides by adding caustic alkali aqueous solutions to mixed aqueous solutions containing manganese and nickel salts, which composite hydroxides are then mixed with lithium compounds and burned at a temperature not less than 600°C and not more than 800°C to make positive active materials represented by a formula $\text{LiNi}_x\text{Mn}(1-x)\text{O}_2$, where the value x is $0,95 \geq x \geq 0,70$; and paste containing the said positive active materials are coated on aluminium foils constituting the positive electrodes of the batteries."

Claims 2, 3, 5 and 6 are dependent claims.

VII. The arguments of the appellants may be summarised as follows.

Both documents D5 as well as D7 may be considered as a proper starting point for the discussion of inventive step. Document D5 discloses the preparation of cathode-active materials based on lithiated nickel compounds optionally including transition metals. According to page 5, lines 4 to 8 of D5, the lithiated nickel dioxide can be obtained by heat treating a substantially homogenous dry intermediate mixture of a

starting material containing nickel hydroxide, hydroxides of cobalt (respectively: manganese) together with LiOH at temperatures above 600°C. Therefore the only feature of independent claims 1 and 4 not disclosed in D5 is the feature defining the formation of the mixed nickel-cobalt (respectively: manganese) hydroxides by coprecipitation. The objective problem which may be defined by this difference is to provide a highly homogeneous structure of the starting material and a good cycling capacity of the electrode material. The importance of the single crystal structure is discussed in the patent specification in column 3, line 56 to column 4, line 1. This is also recognised in document D5, see page 5, lines 35 and 36; and page 6, lines 53 to 58, where the requirement of a uniform composition of the starting material is emphasised. The skilled person would find a solution of the problem to provide a homogeneous structure for the starting materials in document D1, which on page 1, lines 14 to 16 discloses that the electrochemically active material referred to in this document has the same uniform crystal structure throughout. On page 4, lines 22 to 23 of D1 the importance to obtain a uniform product is pointed out. In particular in claim 4 document D1 discloses how this product may be obtained, namely by coprecipitation of a solution containing a nickel salt and a cobalt salt with sodium hydroxide. In carrying out this coprecipitation step the skilled person would obtain a substantially homogeneous starting material as required in the manufacturing process of a positive active material for a lithium secondary battery disclosed in D5, and would hereby carry out the process defined in claim 1 of the patent in suit without an inventive step being involved. With respect to claim 4 of the patent, although document D1 does not disclose the use of manganese in the coprecipitation process, this material is well known as an alternative material to cobalt for secondary batteries and is disclosed in

D5, therefore the skilled person would apply the teaching of D1 equally to coprecipitation of nickel and manganese in order to prepare the nickel-manganese starting material. Claims 7 and 8 of the patent in suit also lack inventive step, because these claims define the application of the active materials of claims 1 and 4 in secondary batteries which is well-known in the art, see document D5, page 3, line 3; and page 8, lines 41 and 42. Finally the use of sulfates as salts in the coprecipitation process is equally known, see for instance document D1, page 2, line 62. Therefore the features of claims 2, 3, 5 and 6 are equally obvious.

In addition, the subject-matter of the claims follows in an obvious way when starting from the disclosure in document D7. In this document a manufacturing process of positive active materials for lithium secondary batteries is disclosed which only differs from the claimed methods in the coprecipitation of nickel and cobalt salts as carbonate salts instead of hydroxides; and in the burning at the temperature of 920°C. The objective problem underlying these differences can be seen in offering an alternative manufacturing process, wherein it should be noted that, since according to the patent in suit homogeneity is important, the alternative process should also result in a homogeneous product. The skilled person would readily find an alternative for the use of nickel and cobalt salts in the coprecipitation process disclosed in document D1. In this respect it is known that the temperature range for burning hydroxides differs from the temperature of 920°C used for burning carbonates in D7. For instance a temperature of 600°C is known from document D5, and a temperature range for burning hydroxides of 600°C to 800°C is acknowledged in the patent specification in the discussion of the prior art (column 2, lines 23 to 27). Therefore the subject-matter of claim 1 is obvious

by the combination of documents D7 and D1, and the further claims are obvious in view of these documents for similar reasons as discussed before.

VIII. The arguments of the respondents may be summarised as follows.

Document D5 discloses a process for producing a cathode-active material wherein a starting material containing a dry mixture of a nickel compound and a transition metal compound is mixed with an aqueous solution of lithium hydroxide in a slurry. This differs from the process in claims 1 and 4 because in the process according to D5 all three components are mixed together in one process step as a result of which the nickel and cobalt particles are in suspension. In contrast in the processes of the patent in suit the nickel and cobalt (respectively manganese) salts are coprecipitated which ensures a single crystal phase. The teaching of D5 furthermore differs from the manufacturing process in the patent by requiring a stoichiometric excess of about 10% to 25% of LiOH. This requirement is motivated by the problem underlying the teaching of D5 which is related to avoiding LiOH or Li_2CO_3 in the end product because of the risk of generating gaseous products in a battery. It is acknowledged that D5 mentions the requirement that the intermediate mixture of LiOH and the starting material should be substantially homogeneous, but this should be interpreted in the context of this disclosure that the mixture is a slurry and that the particles have a mean size between about $1\mu\text{m}$ and $100\mu\text{m}$, which implies that they form a suspension. Since in the process disclosed in D5 all components are mixed and burned together, it would not be obvious to separate the preparation of nickel and cobalt from the mixing with the lithium-component because it could not be predicted which effect this would have on the end product. In

particular the skilled person would not have an incentive to consider the coprecipitation disclosed in document D1, because this document relates to a rather different nickel-metal-hydrid technology in which lithium is not used. Furthermore, D1 teaches to coprecipitate nickel and cobalt compounds for the fabrication of electrodes forming an *end* product, whereas a coprecipitation of these compounds in the process of D5 would be to form the *starting* material, which is therefore not comparable. Finally, since document D5 teaches that hydroxides should be avoided it is not plausible why the skilled person would contemplate applying the teaching of document D1, claim 4, because the coprecipitated nickel and cobalt are in form of hydroxides. Therefore a combination of documents D5 and D1 appears artificial.

With respect to document D7, this document discloses a manufacturing process which is similar to the method of the patent. However, in document D7 the lithium-cobalt-nickel oxide is synthesised by coprecipitation of carbonate salts, which is a completely different process than the synthesis involving hydroxides. Furthermore, from the passage in D7 on page 7, second paragraph wherein it is disclosed that the mixture is burned during three hours at 920°C and then air quenched it is concluded that the crystal structure obtained by burning the carbonates is a rock salt structure. According to document D2, column 1, lines 20 to 25 and line 42, this rock salt structure is an important property of the mixed metal oxides usable as a cathode material, therefore the skilled person would refrain from modifying the process of document D7 with respect to the carbonate salts and the burning temperature. In particular, there is no suggestion in the prior art to modify the coprecipitation process by replacing the mixed metal carbonate salts by metal hydroxides. The coprecipitation process in document D1

involves mixed metal hydroxides but, as discussed before, this document addresses a rather different technology and is completely silent about lithium. In document D5 the cathode material is produced from nickel and cobalt hydroxides, but these are in the form of particles in a suspension and are mixed and burned, and not coprecipitated. Finally document D7 does not refer to the importance of homogeneity of the coprecipitated nickel and cobalt carbonates, therefore it does not suggest to improve the homogeneity by looking for alternative processes such as those in D1 or D5.

Reasons for the Decision

Inventive step

- 1.1 The patent in suit relates to a manufacturing method of positive (cathode) materials comprising mixed metal oxides to be used in lithium secondary batteries. According to the patent specification, see column 2, line 18 to column 3, line 6, in a prior art process based on mixing and burning the cobalt (or manganese), nickel and lithium compounds the discharge capacity of a cathode manufactured in this way decreases in time. The manufacturing process disclosed in the patent is based on coprecipitation, whereby a single phase crystal structure is obtained, as discussed in the passage in column 3, line 56 to column 4, line 1 referred to by the appellant. Therefore in the discussion of inventive step it appears appropriate to start from document D7 which equally teaches a coprecipitation process for the formation of mixed metal lithium cathodes.

2.1 Document D7 discloses in its Example 1 on page 7 of the translation the synthesis of $\text{Li}_x(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ by coprecipitation from an aqueous solution containing Co-ions and Ni-ions as a carbonate salt. The precipitate is mixed with a lithium compound and burned at a temperature of 920°C.

2.2 The subject-matter of claim 1 differs from the manufacturing process in Example 1 of D7 in that composite *hydroxides* are provided through coprecipitation of cobalt and nickel hydroxides by adding caustic alkali aqueous solutions instead of the forming of *carbonates*; and by the burning temperature range of not less than 600°C and not more than 800°C instead of the temperature of 920°C of the process in D7.

The respondents have made reference to document D2 from which it indeed follows that the process conditions in Example 1 of D7 are such that the synthesised material has a rock salt structure, whence it may be concluded that the electrode material produced by the coprecipitation method of D7 has a single phase crystal structure.

2.3 The objective problem solved in claim 1 of the patent in suit can therefore be seen as providing an alternative manufacturing process. In the opinion of the appellants the skilled person, starting from the teaching of document D7, would find an incentive in document D1 for such a modified manufacturing process.

2.4 Document D1, claim 4, indeed defines a coprecipitation of a first solution containing a nickel salt and a cobalt salt; and a second solution comprising sodium hydroxide. However, according to document D1, see column 5, lines 12 to 20, the optimum structure of the cathode material should be *amorphous* rather than having

high crystallinity because amorphous metal hydride compounds show a higher initial capacity as illustrated in Figure 3, curve 1 (low crystallinity product) versus curve 3 (high crystallinity product). In this respect it is noted that the process steps in claim 4 of D1 are appended to those in claim 2, which defines that the pH value should be kept constant in two steps in order to produce the amorphous composition in the coprecipitation process. Therefore the skilled person, looking for an alternative manufacturing process to the process known from document D7, 1st Example, would reject the teaching of document D1, because the teachings of these documents (*amorphous versus crystalline*) would appear to be irreconcilable. Furthermore, as argued by the respondents, it appears questionable whether the teaching of producing an electrochemically active material for a nickel metal hydride battery would be directly applicable to materials for lithium secondary batteries.

2.5 With respect to independent claim 4 which defines a manufacturing process of positive active materials involving manganese it is noted that the process disclosed in document D7 only includes cobalt and that this document is silent about manganese. Also D1 does not disclose manganese. Therefore and for the reasons given in points 2.1 to 2.4 *supra* the subject-matter of claim 4 is not obvious in view of these documents.

3.1 In the opinion of the appellants document D5 could also be considered as closest prior art. This document discloses a manufacturing process of positive active materials for lithium secondary batteries comprising lithium containing oxides, nickel and optionally cobalt or manganese, the material having the formula $\text{Li}_x\text{Ni}_{2-x-y}\text{M}_y\text{O}_2$, wherein x is between about 0.8 and about 1.0; in the case of M=Mn y is less than about 0.2, and in case of M=Co y is less than about 0.5.

3.2 The positive active material defined in claim 1 of the patent in suit differs in the range of composition, because the material according to claim 1 should contain cobalt in a range of 0.05 to 0.5, which mandatory implies the presence of cobalt; whereas the material disclosed in D5 may contain cobalt with a fraction of less than about 0.5, which includes the possibility of no cobalt at all.

Similarly the positive active material from claim 4 of the patent in suit contains manganese with a fractional range of 0.05 and 0.30. According to document D5, the material may contain manganese with a fractional range less than about 0.2, including the case of no manganese being present.

3.3 Therefore, according to document D5 the active material does not have to include cobalt or manganese, as is also illustrated in the Examples I and II. There is also no disclosure in D5 that the presence of these elements or the exact fractional range of them would be related to solving the problem addressed in this document, namely to develop an active material which is free from the evolution of gaseous products during cycling.

3.4 On the other hand, the fractional ranges of cobalt and manganese defined in claims 1 and 4 of the patent in suit contribute to solving the problem of optimising the specific capacity of the positive active material. Although document D5 refers to "improved cycling capacity" in the context of the avoidance of developing gaseous products while cycling (page 4, lines 56 to 57), it does not provide a teaching how the cycling capacity of the active material would be dependent from the fractional composition of cobalt or manganese.

Therefore already these differences, defined in claims 1 and 4 of the patent in suit would appear to contribute to inventive step.

3.5 In the assessment of the board, document D5 also does not give a hint towards the further process steps in claim 1 and claim 4 of the patent, to form *composite hydroxides* comprising nickel and cobalt, or respectively manganese, by coprecipitation. Indeed, following the disclosure of D5 on page 6, lines 27 to 58, the starting material utilizes oxides or hydroxides of nickel and it may *optionally* include oxides or hydroxides of cobalt or manganese. According to page 6, lines 36 and 37, either oxides or hydroxides may be used, because the hydroxides decompose to form oxides when sufficiently heated. It therefore appears that D5 does not express any preference concerning the exact chemical composition of the metals as oxides or hydroxides. Document D5 defines a further requirement that the starting material is desirably in fine particulate form, and most preferably has a mean particle size between about 1µm and about 100µm (page 6, lines 34 and 35). The active material is prepared by contacting the starting material with a saturated solution of lithium hydroxide. The so formed slurry is continually agitated to provide a substantially homogeneous intermediate mixture, which is then burned.

3.6 Therefore document D5 gives an extensive list of the starting materials used in the mixing and burning manufacturing process, namely nickel oxide or hydroxide; *optionally* cobalt oxide or hydroxide; and *optionally* manganese oxide or hydroxide; wherein all these materials are in fine particulate form. This list does not include *composite hydroxides* as defined in claims 1 and 4 of the patent in suit, and there is no obvious reason why the skilled person would consider to

implement a coprecipitation process as defined in claims 1 and 4 of the patent in order to synthesise composite nickel cobalt (or manganese) hydroxides as a starting material for the process in document D5. It is noted that in context of this manufacturing process document D5 refers to "uniform composition" and to the term "homogeneous". These expressions are used, however, to emphasise the need of continuous agitation which, according to this passage of D5, is mandatory when starting from the slurry material.

3.7 As already set out in point 2.4, although document D1 discloses a coprecipitation process, this process results in an electrochemically active material for nickel metal hydride batteries and therefore in a finished product. No obvious reason is seen why the skilled person would use this teaching in order to obtain a starting material for the production of a rather different type of lithium secondary batteries as in D5, the more because according to D5 there is some freedom in the choice of chemical composition and particle size of the starting material, and the inclusion of cobalt and manganese is optional.

4.1 Hence, in the opinion of the board, the subject-matter of claims 1 and 4 is not obtainable by a combination of prior art documents in an obvious way.

4.2 Claims 7 and 8 of the patent in suit define manufacturing processes of lithium secondary batteries including the positive active materials defined in claims 1 and 4, respectively. The subject-matter of these claims include an inventive step for the same reasons as discussed with respect to claims 1 and 4 *supra*.

4.3 Claims 2, 3, 5 and 6 are appended to claims 1 and 4 and equally involve an inventive step.

Order

For these reasons it is decided that:

The appeal is dismissed.

The Registrar:

The Chairman:

P. Martorana

E. Turrini