

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
9 December 2010 (09.12.2010)(10) International Publication Number
WO 2010/139404 A1(51) International Patent Classification:
C01G 51/00 (2006.01) C01G 51/04 (2006.01)

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(21) International Application Number:
PCT/EP2010/003096

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(22) International Filing Date:
19 May 2010 (19.05.2010)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09007465.9 5 June 2009 (05.06.2009) EP
61/184,441 5 June 2009 (05.06.2009) US

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(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK,

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(54) Title: NANOPARTICLE DOPED PRECURSORS FOR STABLE LITHIUM CATHODE MATERIAL

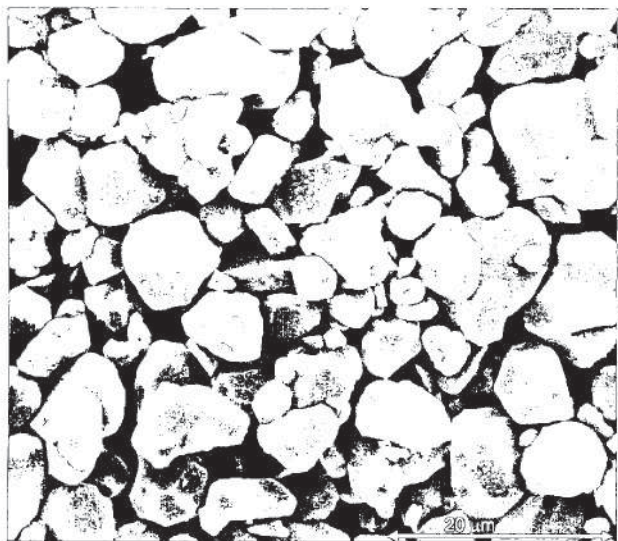


Figure 1a)

(57) Abstract: A precursor compound of a titanium doped lithium cobalt oxide powder consists of either one or more of a non-sintered agglomerated cobalt oxide, hydroxide and oxy-hydroxide powder having a secondary particle size with a d50 of more than 15 μm; said agglomerated cobalt oxide, hydroxide and oxy-hydroxide powder comprising TiO₂ in the form of nanoparticles being homogeneously distributed within said agglomerated powder, with a Ti content of between 0.1 and 0.25 mol%.

WO 2010/139404 A1



SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

Nanoparticle doped precursors for stable lithium cathode material.

The invention relates to precursors for cathode materials for secondary batteries, obtained by the precipitation of heterogeneous metal bearing material, that is homogeneously doped with a nanoparticle metal oxide, metal halide, metal anion, or elemental metal component.

- 5 Compared to Ni-Cd and Ni-MH rechargeable batteries, Li-ion batteries boast an enhanced energy density, mainly due to their higher 3.6 V working voltage. Since their commercialization in 1991 by SONY, Li-ion batteries have seen their volumetric energy density increase continuously. This has been initially realized by optimizing cell design, accommodating more active electrode materials in a fixed volume cell. Later efforts
10 concentrated on improving the energy density of the electrodes. Using a high density active electrode material is another way to achieve this goal. As LiCoO_2 still continues to be used as positive electrode material for the majority of commercial Li-ion batteries, a highly dense variety of this material is in demand.

- In WO2009/003573 such a high density LiCoO_2 material has been disclosed. It provides a
15 relatively coarse-grained electrochemically active LiCoO_2 powder, without significant Li-excess, and having a d_{50} of more than 15 μm , a BET of less than 0.2 m^2/g . The mentioned particle size is evidently a primary particle size, and the particles are neither agglomerated or coagulated, nor aggregated.

- However, this material shows various limitations in a rechargeable lithium battery. One
20 basic limitation originates from the surface area dilemma. Increasing the rate performance (i.e. high power) can be met by increasing the surface area because the solid-state lithium diffusion length can be decreased; which results in an improved rate performance. However, a high surface area increases the area where unwanted side reactions between electrolyte and charged cathode take place. These side reactions are the reason for poor safety, poor
25 cycling stability at elevated voltage and of poor storage properties of charged cathodes at elevated temperature. Furthermore, high surface area materials tend to have a low packing density which reduces the volumetric energy density.

- Recent findings have shown that doping LiCoO_2 cathode materials with different elements, including but not limited to Mg, Ti, Zr, Cr, and Al, has yielded products with improved cycle
30 life, stability, performance, and safety characteristics. The advantages of Ti doping for LiCoO_2 have been mentioned in US6,277,521.

- As for most cathode materials for use in secondary batteries, their preparation often makes use of a particular precursor. The precursor can then be fired with a lithium source to prepare a cathode material. It is therefore important to prepare precursors that can be
35 easily transformed into cathode materials. It is even more beneficial if the precursors can be easily doped with other elements and that the precursor can be used to directly prepare

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the cathode material without additional processing steps. In co-pending application WO2009/074311 various methods for preparing cathode precursor material were discussed, amongst others precipitation, coprecipitation, spray drying, spray pyrolysis, physical mixing or blending, also using slurries. All of these methods have serious problems in achieving good homogeneous doping, especially for Ti doping using a material like nanoparticles of TiO_2 .

As initially said, an essential feature of LiCoO_2 is its high density. The crystallographic density is higher than other cathode materials, namely 5.05 g/cm^3 , and LiCoO_2 shows a good performance even if particles are relatively large and compact. The large and compact particles pack well and thus allow to achieve electrodes with high density. High density electrodes allow to insert a larger mass of active LiCoO_2 into the confined space of a commercial cell. Thus a high density of LiCoO_2 is directly related to a high volumetric density of the final commercial lithium battery. A preferred morphology to achieve high density are compact - mostly monolithic, non-agglomerated - particles. A typical particle size (D50) is at least 10 or even 15 μm , and typically it is less than 25 μm .

There are two major preparation routes to prepare such monolithic LiCoO_2 . In the first route a source of cobalt (like Co_3O_4) with relatively small particle is mixed with a source of lithium (like Li_2CO_3) and fired at sufficient high temperature with a sufficient excess of lithium. During sintering, the small Co_3O_4 particles sinter together and particles grow to the desired size distribution. In the second, alternatively route, relatively large and dense particles of a cobalt source are used. During sintering particles tend to sinter independently. There is a densification within a particle, but not much inter-particle sintering. A problem happens if applying these standard methods to prepare Ti doped LiCoO_2 .

The first method basically results in a failure. If a mixture of TiO_2 , small particles Co_3O_4 and a source of lithium is sintered, by an - to us unknown and surprising mechanism - inter-particle sintering is very much suppressed. As a result a high surface area LiCoO_2 consisting of heavily agglomerated particles is achieved. The preferred morphology mentioned before is only achieved after applying unrealistically high sintering temperature or much larger Li excess. Much higher sintering temperature increases the cost significantly - equipment investment, live time and energy use. Much larger Li excess results in poor performance.

The second obvious method to prepare Ti doped LiCoO_2 is as follows: a relatively dense cobalt precursor (like Co(OH)_2 with large particles size, a source of lithium (like Li_2CO_3) and a source of titanium (like TiO_2) are mixed, followed by sintering. In this case - where the TiO_2 is not well distributed within the particle - we observe an inhomogeneous final product. The reason is that TiO_2 has very poor mobility during sintering, so wherever in the mixture a few TiO_2 particles are agglomerated the final LiCoO_2 will show a region with much higher TiO_2 concentration. As a result, the TiO_2 doping with low doping level (0.1 - 0.5 mol%) is not

efficient. At higher levels a benefit is observed, but because of the poor Ti mobility it is assumed that the inside of the LiCoO_2 particles is basically free of Ti and the full benefit of Ti doping cannot be achieved.

5 A third method to prepare high density TiO_2 doped LiCoO_2 is a two step firing. In a first firing a LiCoO_2 precursor with preferred morphology is prepared. This LiCoO_2 precursor is mixed with TiO_2 , typically at least 0.75 mol% and less than 2 mol% (smaller doping levels are not efficient, the reason is the same as in the second method - any TiO_2 agglomerate will cause a TiO_2 enriched region resulting in a non-homogenous final LiCoO_2). After sintering it is assumed that the LiCoO_2 core is free of TiO_2 and the full benefit of Ti doping is not
10 achieved.

In US2007/0264573 A1 on the other hand an aqueous solution of Mg carbonate, Al and Ti lactate solution is mixed with a Co hydroxide slurry, and after wet ball milling the slurry is spray-dried for granulation. These precursor granules are mixed with Li carbonate and sintered at 1000°C to obtain a Li Co-Mg-Al-Ti oxide. Since it is generally known that such a
15 spray-drying operation is carried out at a temperature below 120°C , and since Ti lactate is a fairly stable compound that will crystallize at such temperatures - since it will only desintegrate to form Ti dioxide at temperatures over 200°C - the spray-dried precursor does not contain TiO_2 in the form of nanoparticles being homogeneously distributed within the precursor.

20 It can further be mentioned that in CN1982219 A a Li Co-Ni-Mn oxide doped with Al, Ti, Mg and/or Cr is obtained by co-deposition, whilst in CN101279771 A a Mg, Al and/or Ti source are mixed in a cobalt nitrate solution which is precipitated as a doped cobalt hydroxide.

It is the scope of the present to provide for a manufacturing method for a cathode material having a high rate performance, showing high stability during extended cycling at high
25 charge voltage, and having a particularly high pellet density. The high temperature storage properties are also to be improved. This can be achieved by the use of precursors that overcome the above mentioned problems in homogeneously distributing dopants in metal hydroxide or oxyhydroxide material.

30 Viewed from a first aspect, the present invention can provide a precursor compound of a titanium doped lithium cobalt oxide powder for use as an active positive electrode material in lithium-ion batteries, said precursor compound consisting of either one or more of a non-sintered agglomerated cobalt oxide, hydroxide and oxy-hydroxide powder having a secondary particle size with a d_{50} of more than $15\text{ }\mu\text{m}$; said agglomerated cobalt oxide,
35 hydroxide and oxy-hydroxide powder comprising TiO_2 in the form of nanoparticles being

homogeneously distributed within said agglomerated powder, with a Ti content of between 0.1 and 0.25 mol%.

In one embodiment, the lithium cobalt oxide powder further comprises Mg as doping
 5 element with a Mg content between 0.1 and 2 mol%. In another embodiment the TiO_2
 nanoparticles have a size range of ≥ 5 nm and ≤ 200 nm, and in still another embodiment
 between 10 and 50 nm.

By 'agglomerated' is understood that the secondary powder particles are decomposed in their
 10 primary particles by applying light to mild forces, like e.g. with soft milling. 'Aggregated'
 powders (also called 'hard agglomerates') on the contrary need excessive force to
 decompose, or cannot be decomposed into their primary particles.

15 Viewed from a second aspect, the present invention can provide the use of the precursor
 compound described before in the manufacture of a lithium cobalt oxide powder for use as
 an active positive electrode material in lithium-ion batteries, said lithium cobalt oxide
 powder having a Ti content of between 0.1 and 0.25 mol%, by firing said precursor with a
 lithium source. In one embodiment, the lithium cobalt oxide powder has a d_{50} of more than
 20 10 μm and in another embodiment more than 15 μm , and in both embodiments a specific
 surface area (BET) of less than 0.25 m^2/g , or even less than 0.20 m^2/g .

Viewed from a third aspect, the present invention can provide a single firing process for
 manufacturing the lithium cobalt oxide powder described before, comprising the steps of:

- 25 - providing for the precursor compound mentioned before,
 - mixing said precursor compound with a Li source, preferably lithium carbonate, according
 to a Li to Co ratio R between 1.04 and 1.07, and
 - firing said mixture with a single firing at a temperature T between 960 °C and 1020 °C.

30 Figure 1a & b: SEM micrograph (2000x magnification) of samples with 0.25 mol% Ti and 0.5
 mol% Mg: Fig. 1a: sample LC0193 (left) and Fig. 1b: LC0227 (right)

Figure 2a & b: SEM micrograph (5000x magnification) of samples with 0.75 mol% Ti and 0.5
 mol% Mg: Fig. 2a: sample LC0199 (left) and Fig. 2b: LC0233 (right)

Figure 3: SEM micrograph of samples without Ti and with 0.5 mol% Mg: sample LC0190 (left)
 35 and LC0223 (right)

Figure 4: Electrochemical performance of undoped LiCoO_2 : sample LC0189. Left: discharge profiles at different rates (from left to right: 3C, C (discharge in 1 hr), C/2, C/10 (each time showing voltage (V) against cathode capacity (mAh/g)); middle: stability (voltage (V) against capacity (mAh/g)- from right to left: Cycle 7, 31 (both at C/10), 8, 32 (both at 1C));

5 right: fade (capacity (mAh/g) against cycle number - line with circles: charge; line with stars: discharge)

Figure 5: Electrochemical performance of LiCoO_2 with 0.25 mol% Ti: sample LC0192 (experiments as described in Fig. 4)

Figure 6a & b: SEM micrograph (2000x magnification) of samples with 0.25 mol% Ti and varying Mg: Fig. 6a: sample LC0322 (left) and Fig. 6b: LC0329 (right)

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Figure 7: Electrochemical performance of LiCoO_2 with 0.25 mol% Ti: sample LC0189 (experiments as described in Fig. 4)

Figure 8: Electrochemical performance of LiCoO_2 with 2 mol% Mg and 0.25 mol% Ti: sample LC0329 (experiments as described in Fig. 4)

15 Figure 9 a & b (top and bottom): Electrochemical performance of LiCoO_2 with 0.2 mol% Ti: samples LC0315 (Fig 9a) and 316 (Fig 9b) (experiments as described in Fig. 4)

Figure 10: Pellet density (g/cm^3) as a function of mean particle size D50 (μm)

Figure 11 a & b: Discharge voltage profiles during extended cycling at 1C (cell voltage against capacity): 11a: sample LC0214 (0.25 mol% Ti); 11b: sample LC0207 (no Ti). For each

20 from right to left: cycles 2, 50, 100, 200, 300 & 500.

The cathode materials for secondary batteries using the type of precursors described before can exhibit an increased stability besides high capacity and energy density, and they can also meet the necessary power requirements, which means that the active cathode material

25 itself and the battery as a whole have a sufficient high rate performance.

An important aspect of the invention is that it can provide precursors of a new type of nanoparticle doped precipitate. In that sense, in a first embodiment a method to incorporate a dopant into a material in which it is usually not stable can be provided. In another embodiment, a method can be provided to dope precipitated materials with

30 insoluble dopants including, such as, but not limited to MgO , Cr_2O_3 , ZrO_2 , Al_2O_3 , or TiO_2 and any general metal oxide, metal halide, metal compound, or elemental metal nanoparticle. In still another embodiment, a method can be provided to introduce a normally unnatural dopant element into a precursor which can later be incorporated into a final material.

Because, for example, TiO_2 is well dispersed within the secondary particles of the precursor compound the diffusion length is short and the cathode material for secondary batteries prepared with this precursor, such as LiCoO_2 , is homogeneous. No region rich in TiO_2 is detected when analysing with EDX. Because of the well distributed Ti already small doping amounts of 0.1-0.25 mol% give the full benefit of Ti doping. Furthermore, by a mechanism that is not yet fully understood - it is surprisingly observed that small Ti doping levels cause a significant increase of pellet density. This is a very desired effect because it allows to increase the volumetric energy density of commercial lithium batteries. Other particular aspects, such as superior rate capability and better stability at high voltage, are illustrated below.

A example of a process used for homogeneously distributing the particulate dopant material in the host materials which are the precursors mentioned before, being composed of primary particles agglomerated into secondary particles, can comprise the steps of:

- providing a first flow comprising a solution of a precursor of the host material,
- providing a second flow comprising a precipitation agent,
- providing a third flow comprising a complexing agent,
- providing a quantity of insoluble particulate dopant material, either in one or more of said first, second and third flows, or in a fourth flow consisting of a suspension of said particulate dopant material, and
- mixing said first, second and third flow, and, if present, said fourth flow, thereby precipitating said host material and said dopant. This process was already detailed in co-pending application PCT/EP2008/010489.

In this example process, the solution of the precursor is preferably an aqueous metal salt solution, and also the suspension of the dopant material is a suspension in water comprising a suspension stabilizing agent. In one embodiment, the particulate dopant material consists of stabilized nanoparticles, such as metals or metal oxides, and the precursor is either one or a mixture of a metal nitrate, chloride, halide, and sulphate powder. In another embodiment, the dopant material is either one or more of MgO , Cr_2O_3 , ZrO_2 , Al_2O_3 , and TiO_2 , and has a size range of ≥ 5 nm and ≤ 200 nm.

As said before, in the example synthesis procedure according to this invention, a feed of insoluble metal oxide nanoparticles can be introduced during the precipitation of a metal hydroxide or oxyhydroxide. It is also possible to introduce the metal oxide nanoparticles into a reactor along with a metal salt solution, an alkaline earth hydroxide, and a complexing agent. In one embodiment, at least two flows of reactants are added to a reactor. At least one of the flows contains a basic composition like NaOH and/or NH_4OH , forming the anion of the precipitate to be obtained, and another flow contains dissolved

metal like CoSO_4 , forming the cation of the precipitate. During the addition of the flows to the reactor, dopant nano-sized particles are present in the reactor. These nano particles are preferably added directly to the reactor or alternatively are fed into any one of the flows, for example in the form of a dispersed solution containing the nano particles, but the
 5 addition can also be in the form of a fine powder. A possible process to dope the precursor with Mg is to provide for a CoSO_4 solution containing the Mg (as MgSO_4) in the desired quantities.

Hence, the following example supply flow schemes to the reactor can be observed:

10

(1) Flow 1: precipitation agent (e.g. NaOH), Flow 2: host material solution (e.g. Mg doped CoSO_4), Flow 3: solution of a complexing agent (e.g. NH_3), Flow 4: Nano dispersion of dopant (e.g. TiO_2)

(2) Flow 1: precipitation agent (e.g. NaOH), Flow 2: host material solution (e.g. Mg doped
 15 CoSO_4), Flow 3: solution of a complexing agent (e.g. NH_3), Nanoparticles: add as a powder to one of the flows or to the mixture of one or more of the Flows 1, 2, 3

(3) Nanoparticles are dispersed in the "starting water" or "starting ammonia" in the reactor, Flow 1: precipitation agent (e.g. NaOH), Flow 2: host material solution (e.g. Mg doped CoSO_4), Flow 3: solution of a complexing agent (e.g. NH_3).

20 After reaction, the precipitated slurry is collected and filtered and the solid is washed with water and then dried to yield metal hydroxide particles doped with nanoparticles. If the precipitate or transition metal ions become oxidized during the reaction or during one of the other processing steps, an oxyhydroxide or oxide of some other chemical composition is obtained.

25 The choice of a soluble metal salt is not restrictive. Soluble metal salts, including nitrates, chlorides, halides, and sulphates may also be used, depending on the application. For the precipitating agents, besides NaOH , for example LiOH , KOH , carbonate, and oxalate salts, may also be used to precipitate the metal salt out of its solution. Complexing agents are for example chosen from soluble amine salts or molecules, including but not limited to NH_3 ,
 30 ethylene diamine tetra-acetate salts, urea, or other known complexing agents. The precipitated host material, for example $\text{Co}(\text{OH})_2$, is usually a hydroxide, but could also be another metal hydroxide, oxide, oxyhydroxide, oxycarbonate, carbonate, or oxalate precipitate that is co-precipitated with the dopant nanoparticles.

The nanoparticle of choice can be of an appropriate size so that it is possible for it to fit
 35 among the primary particles of the host material. In one example there is provided a sufficiently small nanoparticle to allow the nanoparticle to become embedded throughout the $\text{Co}(\text{OH})_2$ particle. In one embodiment the size of the nanoparticle is less than 200 nm

and larger than 10 nm, but nanoparticles of larger or smaller size may be acceptable depending on the composition and morphology of the composite particle required. In general, smaller nanoparticles could be advantageous if deep diffusion into the core of the particle is envisaged.

- 5 The choice of nanoparticle focusses on appropriate size and on the fact that it will not dissolve appreciably, or that it is highly insoluble in the reaction mixture or feed solution that the nanoparticle comes in contact with.

In an embodiment of the invention, a stabilized aqueous solution of TiO_2 nanoparticles, an aqueous solution of cobalt sulphate, caustic, and aqua ammonia are introduced into a
10 stirred and heated reactor and the precipitated material is collected. Thus, crystalline TiO_2 doped $\text{Co}(\text{OH})_2$ is prepared as a Co precursor as used in the second aspect described before.

The reaction can be typically performed using continuous precipitation in an overflow reactor and can be controlled by adjusting and monitoring the pH throughout the experiment. Experiments may also be performed without pH control, by adjusting the feed
15 rates of the reactants. Another possible reaction configuration can be carried out using an autoclave reactor or a batch reactor. The continuous precipitation process is for example performed between 20 °C and 90 °C, but higher or lower temperatures can also be used. An example solvent for the reaction is water, but other solvents, for example glycols, alcohols, acids, and bases can also be used.

- 20 In another example reaction, the pH (temperature uncompensated) is controlled between values of 10.4 to 11.3, or even between 10.8 and 11.0. In general, a higher pH will result in the precipitation of smaller secondary particles, while a lower pH will result in the precipitation of larger secondary particles. The resulting TiO_2 doped $\text{Co}(\text{OH})_2$ can have D50 particle size volume distribution values between 5-50 μm and spans ranging from 0.5 to 2.0.
25 In one example, the steady state production of TiO_2 doped $\text{Co}(\text{OH})_2$ can result in D50 particle sizes ranging from 6-21 μm with spans ranging from 0.9 to 1.3. The span is defined as being $(\text{D90}-\text{D10})/\text{D50}$.

The primary platelet sizes of the precipitated TiO_2 doped $\text{Co}(\text{OH})_2$ can range from 10 nm to 2000 nm, with typical primary platelet sizes being for example between 50-400 nm. The tap
30 density of the TiO_2 doped $\text{Co}(\text{OH})_2$ can range from 0.7-1.5 g/cm^3 and is for example between 1.2-1.5 g/cm^3 . In general, larger TiO_2 doped $\text{Co}(\text{OH})_2$ secondary particles and primary particle thicknesses can give higher tap densities. The apparent density of this material can range from 0.3-1.2, for example with typical values of 0.8-1.2 g/cm^3 .

The precipitated TiO_2 doped $\text{Co}(\text{OH})_2$ powder is for example a composite of two separate
35 phases: one of TiO_2 and one of $\text{Co}(\text{OH})_2$. The composite particles can usually be composed of collections of primary particles of $\text{Co}(\text{OH})_2$, with thicknesses that can be between 20-500 nm, for example between 50-200 nm. Interdigitated and embedded between the primary

platelets of Co(OH)_2 are the TiO_2 nanoparticles. The TiO_2 is embedded throughout the Co(OH)_2 particle and is not solely on the surface of the particle.

The composite secondary particles typically can have a D50 range between 1-50 μm and more typically between 5-25 μm . It is during the precipitation that the PSD is typically
5 controlled, although precipitated material can also be prepared using a gel preparation and then processed to a smaller size. Other processing methods, including grinding, milling, or other attrition techniques, may be used to prepare particles of appropriate size.

With the example aggregated precursor according to the first aspect above, using a suitable blending ratio of Li to Co, and a single firing step, the primary particles in the end product
10 grow larger, while there is little change in secondary particle size. Under certain conditions, such as with a blending ratio of Li to Co between 1.04 and 1.07, and a firing temperature in the range of 960 to 1020 $^\circ\text{C}$, the primary particles forming the secondary structure can indeed grow together. In this way, and by using aggregated Co(OH)_2 , the final lithium cobalt oxide powder can be prepared cost effectively.

15 The example precursor product can thus be defined as either one or more of a non-sintered agglomerated powdery cobalt oxide, hydroxide and oxy-hydroxide, having a secondary particle size with a d50 of more than 15 μm . In one embodiment the primary particles have a primary particle size with a d50 of less than 5 μm . The secondary particles can have a spherical shape. The cobalt oxide can either be Co_3O_4 , Co_2O_3 , or a partially oxidized and
20 dried Co(OH)_2 . It is an advantage when the secondary particles of the precursor do not contain any sintered primary particles, since the desired result is normally obtained using a single firing step.

25 The invention may be illustrated by the following experimental details:

Preparation of Mg and/or Ti doped precipitated hydroxide

A series of in total 12 cobalt hydroxide based precursors are prepared in a small pilot plant continuous precipitation line using the process described above. A flow of TiO_2 nano
particles is continuously fed into the reactor, and at the same time Mg-doped Co-sulfate
30 solution, sodium hydroxide solution and NH_4OH are added continuously to the reactor. Precipitated samples are collected after reaching steady state. Each preparation takes more than one week. After sampling the cobalt based hydroxide is washed and dried.
The intention of this series is to prepare precursors with similar morphology but different doping. TiO_2 doping levels (per 1 mol Co) range from 0 to 0.75 mol%. Mg doping levels per
35 mol Co vary between 0 and 2 mol%.

ICP elemental analysis confirms that the targeted composition is achieved for all of these samples. Great care is taken to ensure that the morphology of all these precursors is very similar. All precursors have a tap density ranging from 1.35 - 1.45 g/cm³ and the D50 (particle size distribution, wet method) of 17-21 μm . Morphology, checked by SEM, looks very similar, showing irregular secondary particles consisting of slightly coarse primary plate-shaped particles. The TiO₂ containing samples have the TiO₂ well distributed within the secondary particles.

Preparation of Mg and/or Ti doped LiCoO₂

More than 36 final LiCoO₂ base samples are prepared from these precursors as follows:

10 The cobalt hydroxide based precursor is mixed with fine Li₂CO₃ particles, then fired in dry air at 1015°C, followed by milling and sieving. Typical sample size is 1 kg. The Li:Co molar blend ratio varies from 1.04 to 1.07.

The final samples are investigated by particle size analysis (PSD, dry method), BET surface area, SEM microscopy, coin cell testing, pH titration and pellet density. Selected samples are further tested by elemental analysis (ICP), full cell testing (commercial size Li polymer cells, including safety tests, storage tests and cycling stability test), electrode density, EDX cross section, DSC safety estimation etc.

Particle size distribution of LiCoO₂ is measured using laser diffraction. A standard analysis of laser diffraction particle analysis assumes that the particles which created the diffraction pattern are spheres with various volume. The "D50" is median of the size-volume distribution, i.e. particles with smaller size contribute 50% to the total volume. Correspondingly, "D10" and "D90" are the size where smaller particles contribute 10% or 90% to the total volume.

The specific surface area of LiCoO₂ is measured with the Brunauer-Emmett-Teller (BET) 5 point method using a Micromeritics Tristar.

Pellet density is measured as follows: 3g of powder is filled into a press from with a diameter of 1.292 cm. Pressure is applied for 30 sec, whereupon the powder sample thickness is measured. By knowing its pressed volume and weight the pellet density is calculated.

30 Electrochemical performance is tested in coin type cells, with a Li foil as counter electrode in a lithium hexafluorite (LiPF₆) type electrolyte at 25 °C. Cells are charged to 4.3 V and discharged to 3.0 V to measure rate performance and capacity. The capacity retention during extended cycling is measured at 4.5V charge voltage. Specific capacity of 160 mAh/g is assumed for the determination of the discharge rates. For example, for discharge at 2 C, a specific current of 320 mA/g is used.

Rate capability is measured at different discharge rates (as in Fig.4, left):

11

Cycle 1: C/10, 2: C/5, 3: C/2, 4: 1C, 5: 2C, 6: 3C (1C = 160 mA/g)

For stability and fade measurements (as in Fig. 4, middle and right), the cycling procedure is continued as follows:

Cycle 7: C/10

5 Cycle 8: 1C

Cycles 9 to 30: cycled at C/4 charge and C/2 discharge at 4.5-3.0 V

Cycle 31: C/10

Cycle 32: 1C

10 Good materials should at least have the following properties:

- BET: Small BET surface area, typically below 0.25 or even 0.2 m²/g

- SEM: Preferred are powders comprising dense, compact, monolithic secondary particles - thus avoiding excessive agglomerates

- Coin cell testing showing:

15 (a) high rate performance

(b) rectangular shape of discharge profile at higher rate

(c) small change of voltage profile after extended cycling at 4.5V

(d) high capacity retention during extended cycling stability at 4.5V

- Pellet density: as high as possible

20 - PSD: no excessive number of large or small particles, or Low span $(=(D_{90}-D_{10})/D_{50})$ and monomodal PSD.

The surprising discovery is made that very small amounts of titanium (much below 0.5 mol%) dramatically improve the performance (pellet density, rate performance, cycling stability) without sacrificing any other positive property. Also, if the Ti doping level exceeds 0.5

25 mol%, then it is impossible to obtain the preferred morphology. The particles have high BET surface and are strongly agglomerated. We furthermore discovered that the benefit of Ti is completely independent of magnesium doping level.

Generally, the best performance is achieved with 0.25 mol% TiO₂ doping or less. In the presence of TiO₂, introducing additional magnesium doping causes a small decrease of capacity without losing rate performance, but gaining in safety performance. In the

30 following aspects of the invention are described by examples:

Example 1

Two cobalt hydroxide precursors, doped with 0.5 mol% Mg and containing 0.25 mol% dispersed TiO₂ nano particles are used to prepare 6 final LiCoO₂ based samples.

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The sintering temperature is 1015°C, and the Li:Co molar ratio of the blend is varied between 1.04 and 1.07. Note that this ratio does not correspond to the true Li:Co ratio of the final sample (which is smaller by about 2-4%).

Table 1 summarizes the obtained results:

Sample info		Physical				Coin Cell (Half Cell) Testing:				
Sample	Li:Co blend	BET m ² /g	PD g/cm ³	PSD		DC Q mAh/g	Q _{irr} %	Rate (versus 0.1C)		
				D50	SPAN			1C(%)	2C(%)	3C(%)
LC0191	1.04:1	0.234	3.627	13.74	1.71	157.89	0.84	95.47	93.47	92.20
LC0226		0.233	3.635	12.90	1.46	157.92	2.58	95.23	93.07	91.84
LC0192	1.055:1	0.207	3.679	15.79	1.44	156.21	3.21	94.32	91.84	90.02
LC0227		0.195	3.718	17.23	1.32	155.23	3.71	92.92	89.91	87.77
LC0193	1.07:1	0.176	3.755	20.14	1.42	154.90	4.46	92.44	89.26	87.13
LC0228		0.171	3.777	23.33	1.25	153.63	4.60	91.12	87.26	84.57

5 PD: pellet density; DC Q: discharge capacity;

Q_{irr} (irreversible capacity) = $[Q_{\text{charge}} - Q_{\text{dc}}] / Q_{\text{charge}}$ (in %) of the first cycle, measured at C/10 rate.

10 All samples have excellent performances. The BET decreases with particle size, and the pellet density increases. Particularly LC0227 and LC0193 are of interest. They offer the best compromise between desired particle size, good electrochemical performance and very high pellet density. Figure 1 shows the SEM micrograph of samples LC0227 and LC0193. We observe quite compact particles with some edges and faces. This morphology is especially preferred to obtain high density.

15

Counterexample 2

Two cobalt hydroxide precursors, doped with 0.5 mol% Mg, containing 0.75 mol% dispersed TiO₂ nano particles are used to prepare 6 final LiCoO₂ based samples. Sintering conditions are as in Example 1.

5 Table 2 summarizes the obtained results:

Sample info		Physical				Coin Cell (Half Cell) Testing:				
Sample	Li:Co blend	BET m ² /g	PD g/cm ³	PSD		DC Q mAh/g	Qirr %	Rate (versus 0.1C)		
				D50	SPAN			1C (%)	2C (%)	3C(%)
LC0197	1.04:1	0.399	na	11.18	1.88	158.80	0.84	98.26	97.37	96.64
LC0232		0.543	na	11.93	1.86	157.89	2.55	98.04	96.73	95.69
LC0198	1.055:1	0.313	na	10.96	1.74	157.55	1.96	97.54	96.26	95.24
LC0233		0.428	na	12.58	1.83	157.84	2.48	98.17	97.06	96.27
LC0199	1.07:1	0.342	(3.587)	10.75	2.04	157.61	2.17	96.55	95.13	93.96
LC0234		0.320	(3.596)	13.49	1.88	157.31	2.62	97.59	96.16	95.17

The main difference with the 0.25 mol% Ti doped samples of Example 1 is that the BET is very large, and the particle size much smaller. With increasing Li:Co, the BET does not decrease much, and the particle size increases insignificantly. Pellet density could not be measured reliable, because of strong agglomeration, as will be discussed next.

Figure 2 shows the SEM micrograph of 2 typical samples, LC0199 and LC0233. Note that the magnification is different from Figure 1t! Obviously, the morphology of these samples, doped with 0.75 mol% Ti is very different from the 0.25 mol% doped samples. The first are strongly agglomerated, with small primary crystallites ranging from sub-micrometer to 5 µm, the latter are large and compact, primary crystallites have about 5-20 µm size.

The strong agglomeration is the reason that pellet density could not be measured reliable, simply because the agglomerates are breaking under the applied force, giving results that are much too high for the given morphology. Values of 3.59 are measured (the realistic value is smaller), much below those of Example 1.

6 more samples are prepared using 0.5 mol% Mg doped Cobalt hydroxide, additionally containing 0.5 mol% Ti. The results are in between those of Example 1 and Counterexample 2; showing clearly more agglomerated, lower density and higher BET than those of Example 1.

It is concluded that doping of LiCoO₂ with more than about 0.25 mol% Ti is undesired.

Counterexample 3

Two cobalt hydroxide precursors, doped with 0.5 mol% Mg without containing dispersed TiO_2 nano particles are used to prepare 6 final LiCoO_2 based samples. Sintering conditions are as in Example 1.

5 Table 3 summarizes the results:

Sample info		Physical				Coin Cell (Half Cell) Testing:				
Sample	Li:Co blend	BET m ² /g	PD g/cm ³	PSD		DC Q mAh/g	Qirr %	Rate (versus 0.1C)		
				D50	SPAN			1C (%)	2C (%)	3C(%)
LC0188	1.04:1	0.260	3.532	11.52	1.44	158.81	0.84	97.10	95.30	93.58
LC0223		0.174	3.598	17.34	1.19	156.29	3.44	93.22	90.44	88.58
LC0189	1.055:1	0.216	3.513	13.58	1.28	158.10	2.76	95.37	93.25	91.65
LC0224		0.133	3.734	26.02	1.31	152.94	5.37	90.75	87.12	84.83
LC0190	1.07:1	0.178	3.627	16.87	1.23	156.69	3.72	93.74	91.04	89.18
LC0225		0.110	3.805	34.66	1.20	150.53	6.47	88.75	84.34	81.65

The main difference with Example 1, at similar particle size, is to be found in a much larger pellet density. Figure 3 shows the SEM micrograph of samples LC0190 and LC0223. The particles are compact, the particle size is comparable, but compared with 0.25 mol% Ti of Example 1, the shape is very different. The shape is more round and sometimes concave. This morphology is less preferred and results in a much lower pellet density for an identical size.

Furthermore, the rate performance and stability of 0.25 mol% Ti doped samples of Example 1 is much superior. The numeric values are not so different, but a careful look at the voltage profiles during cycling and rate performance shows very clear differences.

Figure 4 shows the performance of a typical undoped sample and compares with a 0.25 mol% Ti doped sample. Both samples have quite similar key parameters (PSD, BET, ...). The profile of 0.25 mol% Ti doped samples, especially at high rate, is much more rectangular - more steep at the end of discharge - and it remains more rectangular during cycling, whereas undoped samples show a clear deterioration of discharge voltage profile. A decrease in fading rate for the 0.25 mol% doped samples is also observed, whereas the TiO_2 free sample continues to loose capacity. We conclude that LiCoO_2 without the inventive Ti doping has less cycle stability and lower rate performance.

Example 4

Two cobalt hydroxide precursors, undoped or doped with 2 mol% Mg, and also containing 0.25 mol% dispersed TiO₂ nano particles, are used to prepare 12 final LiCoO₂ samples. Sintering conditions are as in Example 1.

5 Table 4 summarizes the results.

Sample info			Physical				Coin Cell (Half Cell) Testing:				
Sample	Comment		BET m ² /g	PD g/cm ³	PSD		DC Q mAh/g	Qirr %	Rate (versus 0.1C)		
	Mg mol %	Li:Co Blend			D50	SPAN			1C(%)	2C(%)	3C(%)
LC0321	0	1.04	0.221	3.703	14.43	1.67	158.91	2.34	97.08	95.29	93.85
LC0322		1.055	0.194	3.767	16.77	1.50	157.78	3.21	95.15	92.64	90.79
LC0323		1.07	0.188	3.777	17.41	1.47	157.33	3.37	94.65	92.04	90.09
LC0191	0.25	1.04	0.234	3.627	13.74	1.71	157.89	2.43	95.47	93.47	92.20
LC0192		1.055	0.207	3.679	15.79	1.44	156.21	3.21	94.32	91.84	90.02
LC0193		1.07	0.176	3.755	20.14	1.42	154.90	4.46	92.44	89.26	87.13
LC0226		1.04	0.233	3.635	12.90	1.46	157.92	2.58	95.23	93.07	91.84
LC0227		1.055	0.195	3.718	17.23	1.32	155.23	3.71	92.92	89.91	87.77
LC0228		1.07	0.171	3.777	23.33	1.25	153.63	4.60	91.12	87.26	84.57
LC0327	2.0	1.04	0.203	3.639	15.87	1.50	154.73	4.85	93.99	91.72	89.95
LC0328		1.055	0.199	3.645	15.98	1.49	153.82	5.42	92.62	90.13	88.28
LC0329		1.07	0.176	3.703	18.00	1.30	152.06	6.73	90.77	87.66	85.65

All samples exhibit a high pellet density. All samples showed a similar sintering behaviour that those of Example 1. Figure 6 (SEM of samples LC0322 & 329) shows that excessive agglomerated morphology, observed for larger Ti doping as in Counterexample 2, is absent.

- 10 The morphology is quite similar to those of Example 1. Figure 7 and 8 show a similar cycling performance as observed in Example 1. We conclude that Mg content has very little influence on the morphology. Typical is the rectangular voltage at higher rate, remaining rectangular also after extended cycling. The reversible capacity, however, decreases slightly with increasing Mg doping - this is generally observed for Mg doped LCO.

15 Counterexample 5

A cobalt hydroxide precursor, doped with 2 mol% Mg and containing 0.5 mol% dispersed TiO₂ nano particles is used to prepare 3 final LiCoO₂ samples. The preferred morphology - as described in Ex. 1- is not obtained. The samples show excessive agglomeration, similar to

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Counterexample 2. Counterexample 5 confirms that a well controlled Ti doping level is important for morphology, but Mg doping is not.

Counterexample 6

0.20 mol% Ti (as TiO_2) is added to a LiCoO_2 sample having preferred morphology. The
5 TiO_2 - dry coated LiCoO_2 is heated at 1015°C in air, resulting in samples LC0315 & 316. Pellet
density did not increase. Samples of Example 1 or 4 have - at similar particle size -
significantly higher pellet density. Figures 9a and 9b show that the voltage profile is much
less rectangular than that of samples of Example 1 and 4. This Counterexample shows that Ti
needs to be finely dispersed within the precursor. If it is added on the outside of the sample
10 a much higher Ti doping is needed before a clear beneficial effect is observed.

Counterexample 7

This example shows that Ti doped LiCoO_2 - prepared from a standard precursor different
from the composite material of this patent - involves severe problems. The precursor is
15 Co_3O_4 , doped with 1 mol% magnesium per 1 mol cobalt, Li_2CO_3 (same batch like used for all
other examples and counter examples, and TiO_2 sub-micrometer powder (uncoated
pigment).

First a well-homogenized pre-blend containing a fraction of the Co_3O_4 and all TiO_2 (the TiO_2
is carefully pre-dried), is prepared, this blend is added to the remaining Co_3O_4 and Li_2CO_3
20 and blending is continued. The final blend does not contain any visible agglomerates of TiO_2
or Li_2CO_3 . The final blend contains 0.25 mol% TiO_2 per 1 mol Co.

A total of 4 blends with Li:Co ratios ranging from 1.054 to 1.072 are used, firing at 1000°C
results in Ti + Mg doped LiCoO_2 . The obtained particle size is significantly smaller (10-15 μm)
than expected for similar Li:Co blend ratios without TiO_2 . As a comparison - using the same
25 Co_3O_4 precursor, the same firing conditions and the same Li:Co blend ratios yields particle
sizes ranging from 24 - 35 μm . This shows that it is not possible to obtain a preferred
morphology (PSD of 15-20 μm) without using excessive high Li:Co blend ratios or excessive
high sintering temperature.

Particle size results are summarized in the following Table 5:

Sample info			PSD Laser diffraction (dry, H ₂ O)							
Sample	Li:Co (mol)		< 1µm (%)	< 3µm (%)	Dmin µm	D10 µm	D50 µm	D90 µm	D100 µm	Span
LC0345	1.054	0.25 mol% Ti	0.00	0.12	2.91	5.58	10.59	19.95	44.81	1.36
LC0346	1.058		0.00	0.00	3.48	6.43	12.25	23.26	52.31	1.37
LC0347	1.068		0.00	0.00	3.48	6.43	12.25	23.26	52.31	1.37
LC0348	1.072		0.00	0.00	3.48	6.43	12.25	23.26	52.31	1.37
LC0181	1.052	No Ti	0.00	0.43	2.04	11.88	23.77	43.25	71.23	1.32
LC0182	1.057		0.00	0.00	8.48	15.12	27.69	48.65	81.81	1.21
LC0163	1.068		0.00	0.23	2.43	19.05	35.73	61.19	96.41	1.18
LC0164	1.072		0.00	0.15	2.91	20.79	36.52	60.29	96.36	1.08

- The underlying mechanism is possibly the following: TiO₂ is very efficient to prevent sintering by inter particle sintering, as a result there is less growth of particle size. Thus - in order to obtain Ti doped LiCoO₂ with preferred morphology - i.e. having larger and compact particles requires that the TiO₂ is finely dispersed within larger sized precursor particles, as described in this invention.

Example 8

- Figure 10 shows the pellet density as function of particle size D50. The samples on the upper dotted line have Mg contents from 0 to 2 mol%, and Ti content of 0.25 mol%. The samples on the lower dotted line have a Ti content of 0, 0.5 and 0.75 mol%, and 0.5 to 2 mol% Mg. No sample without titanium has a sufficient high pellet density. Of the samples with high pellet density only those with 0.25 mol% precursor doping have a preferred morphology. Example 8 clearly shows the benefit of titanium doping for obtaining increased pellet density.

Example 9

- The large pool of samples with 0% Ti doping and 0.25mol% Ti doping is analyzed in order to understand how to prepare basically identical samples (morphology, PSD, lithium:Co ratio, BET, ..) mainly differing by Ti content only. Additionally, the Ti doped sample has a significantly higher pellet density.

Table 6 summarizes the properties.

Preparation				Physical				PSD RTC Dry							
Sample	Ti mol%	Li:Co Blend	T sint oC	BET m ² /g	Tap g/cm ³	Pellet g/cm ³	H ₂ O ppm	<1 %	<3 %	Dmin um	D10 um	D50 um	D90 um	D100 um	Span
LC0207	0.0	1.055	1005	0.255	2.40	3.521	80.00	0.00	0.98	1.42	5.99	12.70	24.6	46.1	1.46
LC0214	0.25	1.045	1015	0.276	2.43	3.674	90.00	0.00	3.67	1.42	4.47	12.88	28.9	60.5	1.89

Full cells testing shows an clearly improved stability of the Ti doped sample during extended cycling (> 500 cycles). The TiO₂ doped sample, compared with an undoped reference, shows
 5 clearly less voltage depression (=unwanted impedance), especially at the beginning of discharge. At the same time, the capacity fading rate is clearly improved. Figures 11a and b illustrate this, for resp. Samples LC0 214 and 207.

While specific embodiments and/or details of the invention have been shown and described
 10 above to illustrate the application of the principles of the invention, it is understood that this invention may be embodied as more fully described in the claims, or as otherwise known by those skilled in the art (including any and all equivalents), without departing from such principles.

Claims

1. Precursor compound of a titanium doped lithium cobalt oxide powder for use as an active positive electrode material in lithium-ion batteries, said precursor compound consisting of
5 either one or more of a non-sintered agglomerated cobalt oxide, hydroxide and oxy-hydroxide powder having a secondary particle size with a d50 of more than 15 μm ; said agglomerated cobalt oxide, hydroxide and oxy-hydroxide powder comprising TiO_2 in the form of nanoparticles being homogeneously distributed within said agglomerated powder, with a Ti content of between 0.1 and 0.25 mol%.
- 10 2. Precursor compound according to claim 1, characterized in that said lithium cobalt oxide powder further comprises Mg as doping element with a Mg content between 0.1 and 2 mol%.
- 15 3. Precursor compound according to claims 1 or 2, characterized in that said TiO_2 nanoparticles have a size range of ≥ 5 nm and ≤ 200 nm, and preferably between 10 and 50 nm.
- 20 4. Use of a precursor compound according to any one of claims 1 to 3 in the manufacture of a lithium cobalt oxide powder for use as an active positive electrode material in lithium-ion batteries, said lithium cobalt oxide powder having a Ti content of between 0.1 and 0.25 mol%, by firing said precursor with a lithium source.
- 25 5. Use according to claim 4, wherein said lithium cobalt oxide powder has a d50 of more than 10 μm , preferably more than 15 μm , and a specific surface area (BET) of less than 0.25 m^2/g , and preferably 0.20 m^2/g .
6. Single firing process for manufacturing a lithium cobalt oxide powder, comprising the steps of:
- providing for a precursor compound according to any one of claims 1 to 3,
 - 30 - mixing said precursor compound with a Li source, preferably lithium carbonate, according to a Li to Co ratio R between 1.04 and 1.07, and
 - firing said mixture with a single firing at a temperature T between 960 °C and 1020 °C.

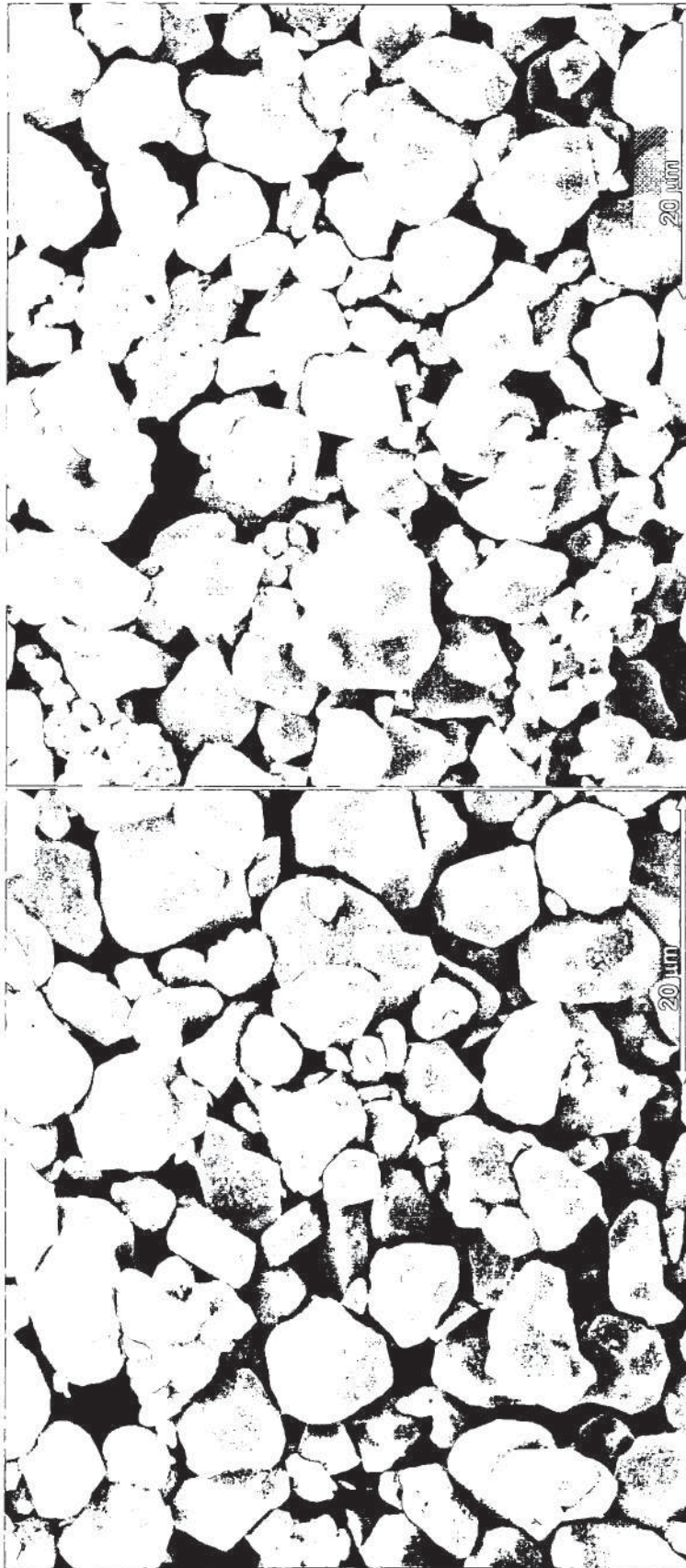


Figure 1b)

Figure 1a)

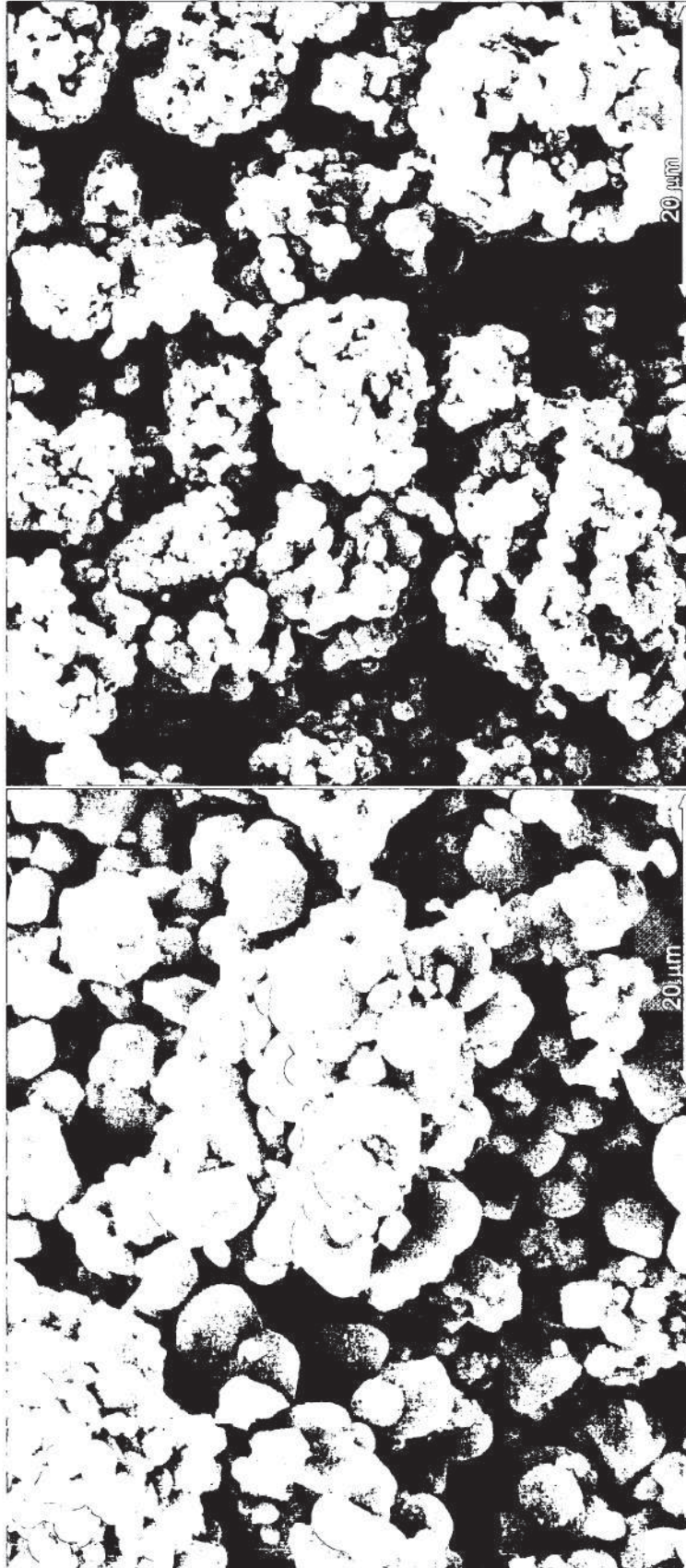


Figure 2b)

Figure 2a)



Figure 3b)

Figure 3a)

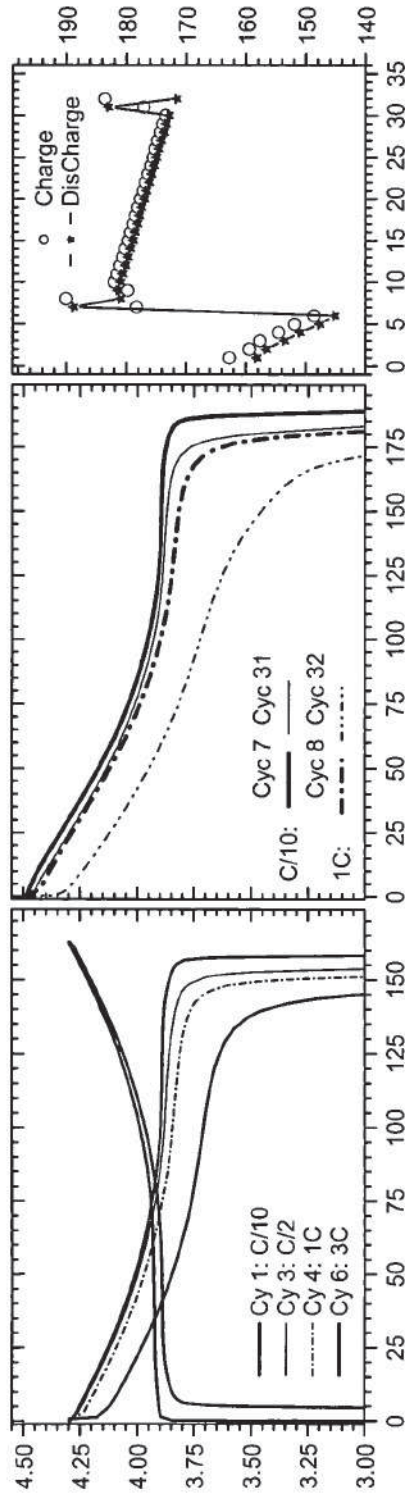


Figure 4)

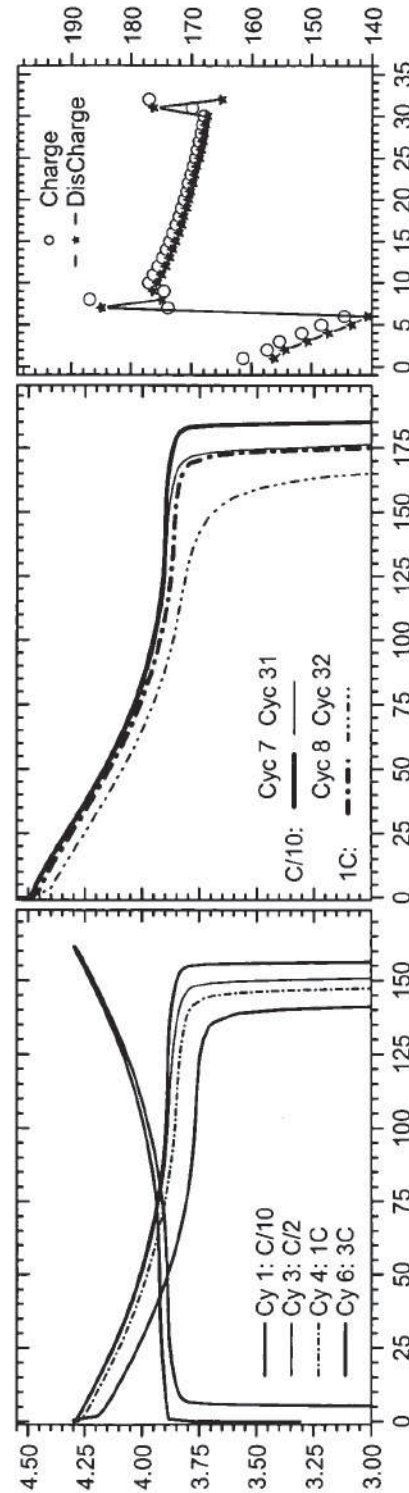


Figure 5)

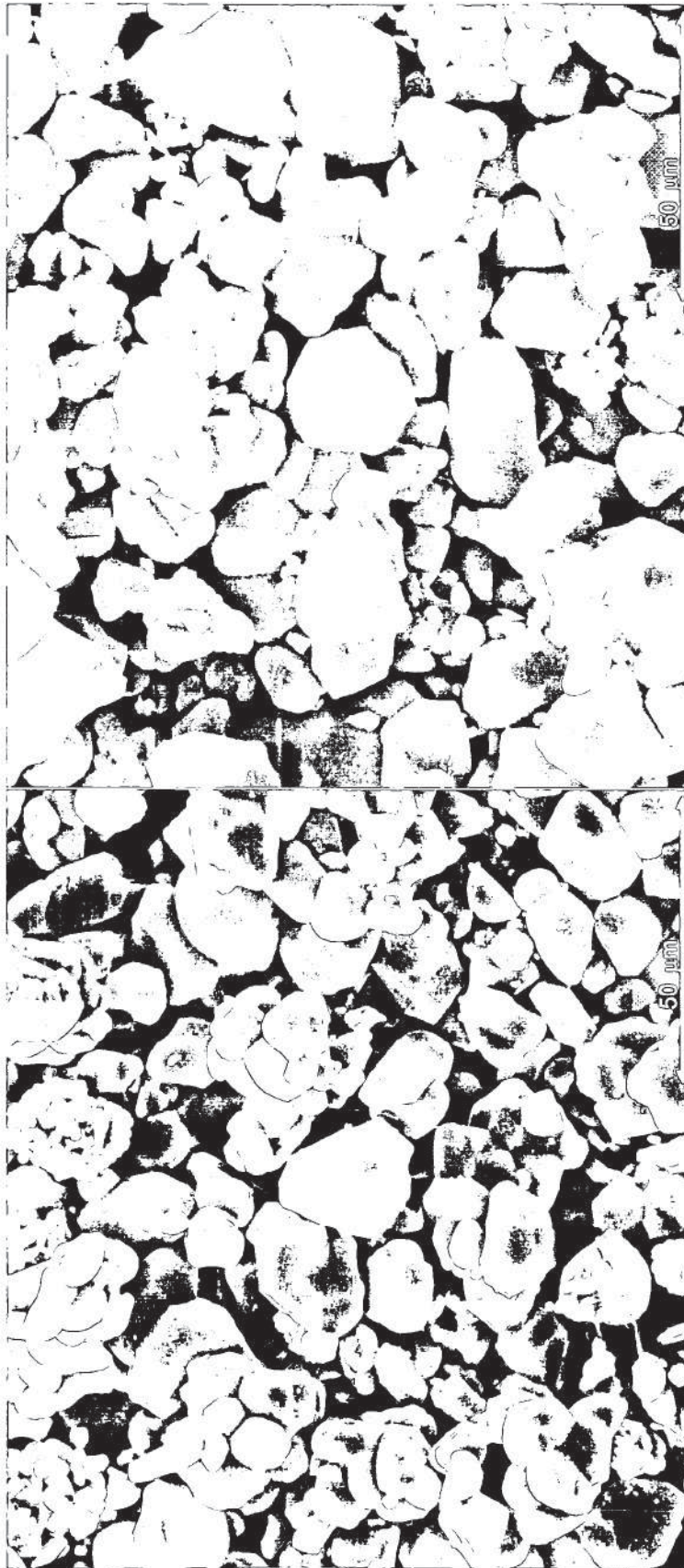


Figure 6b)

Figure 6a)

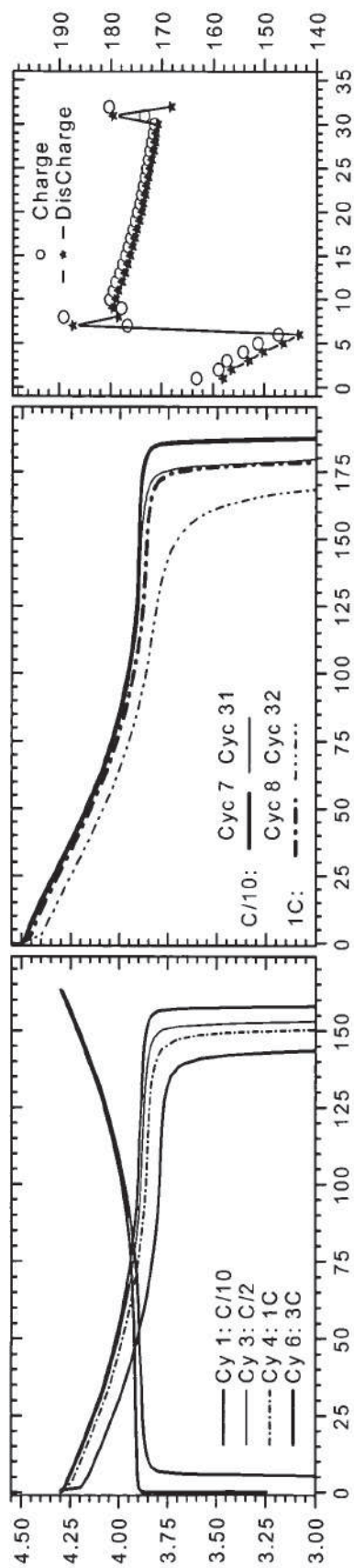


Figure 7)

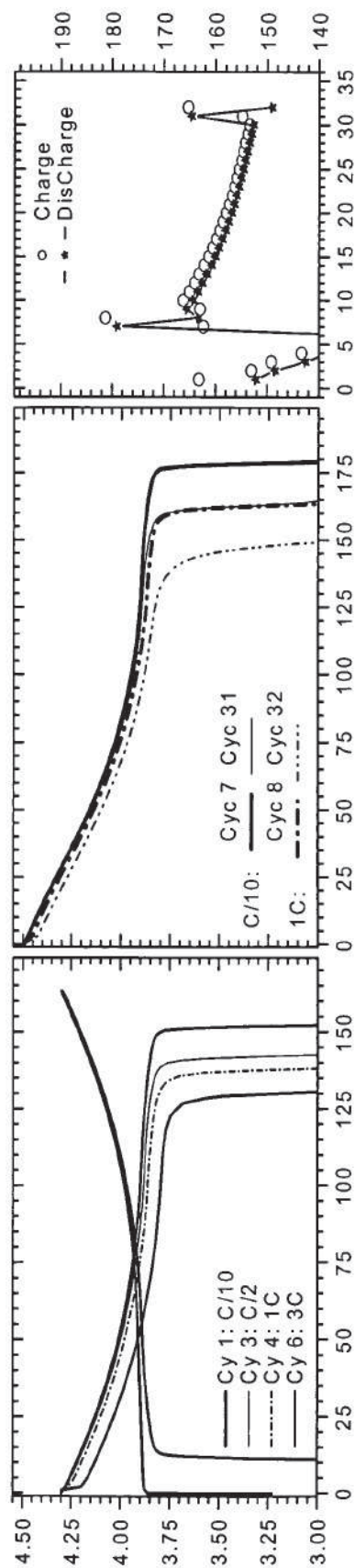


Figure 8)

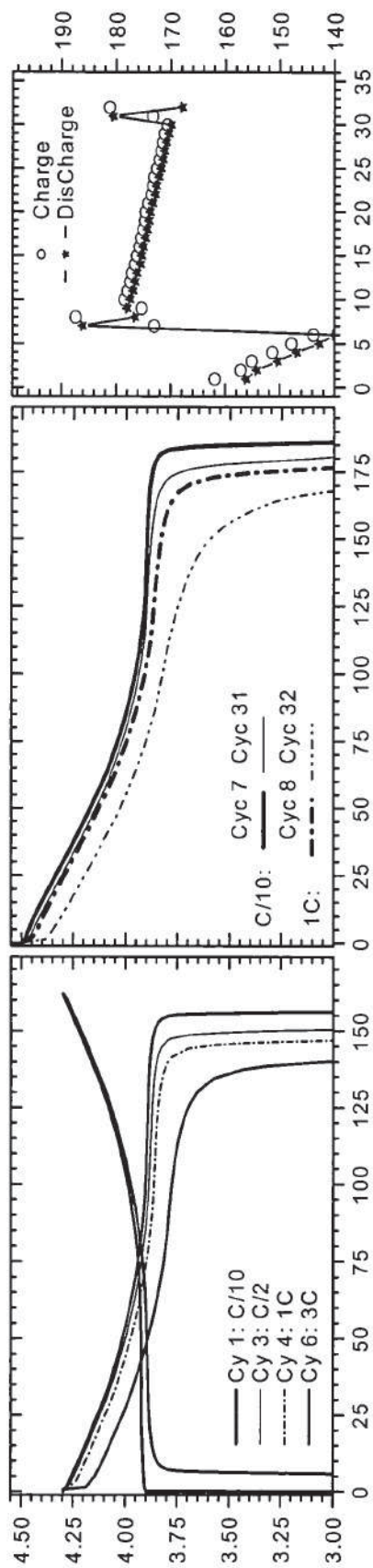


Figure 9a)

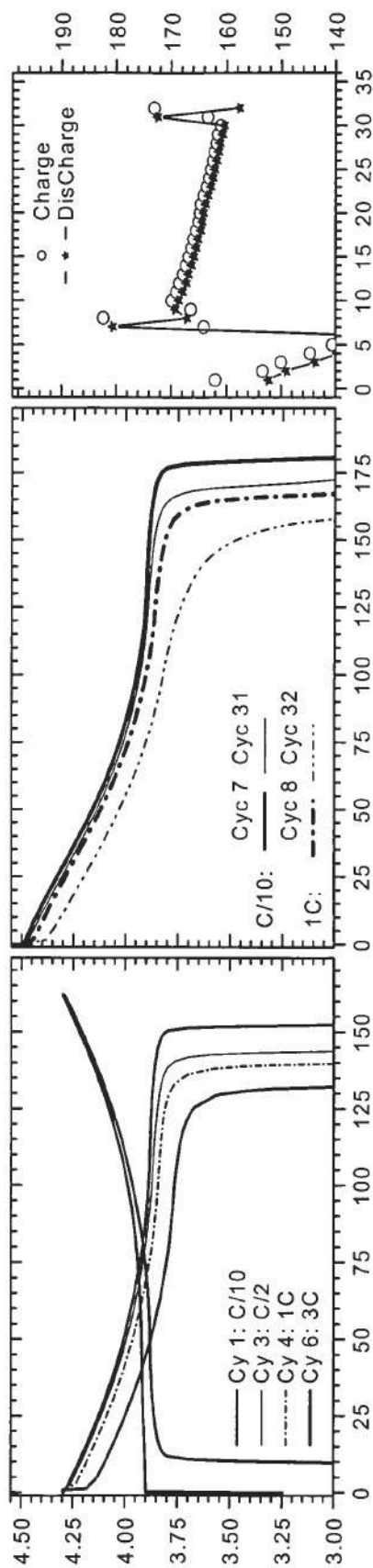


Figure 9b)

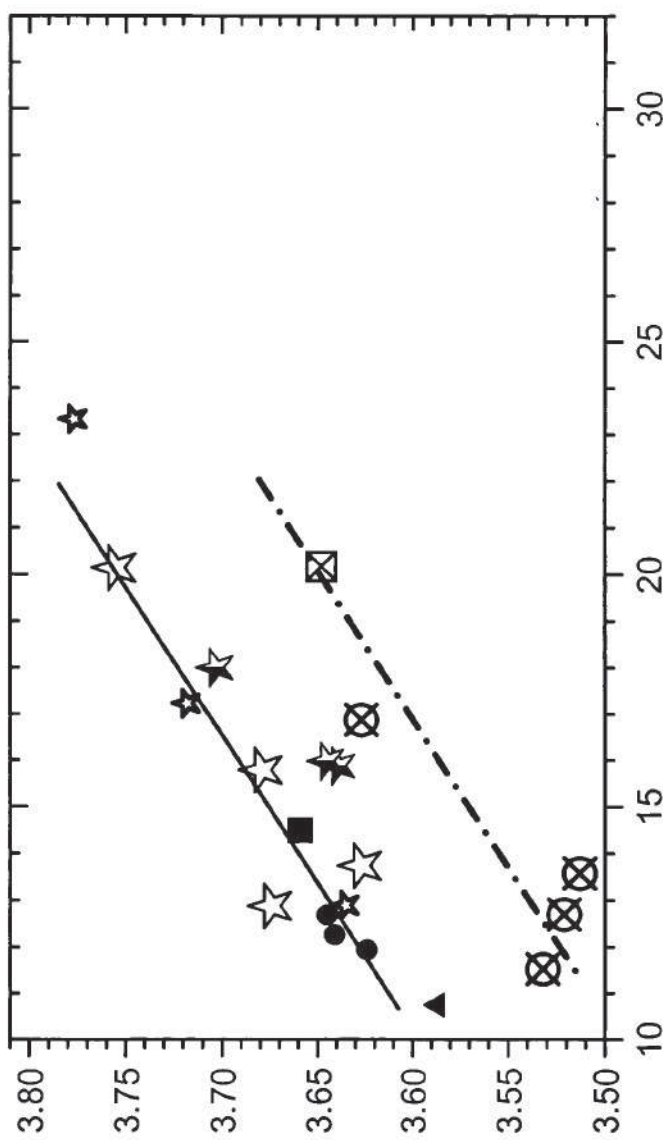


Figure 10)

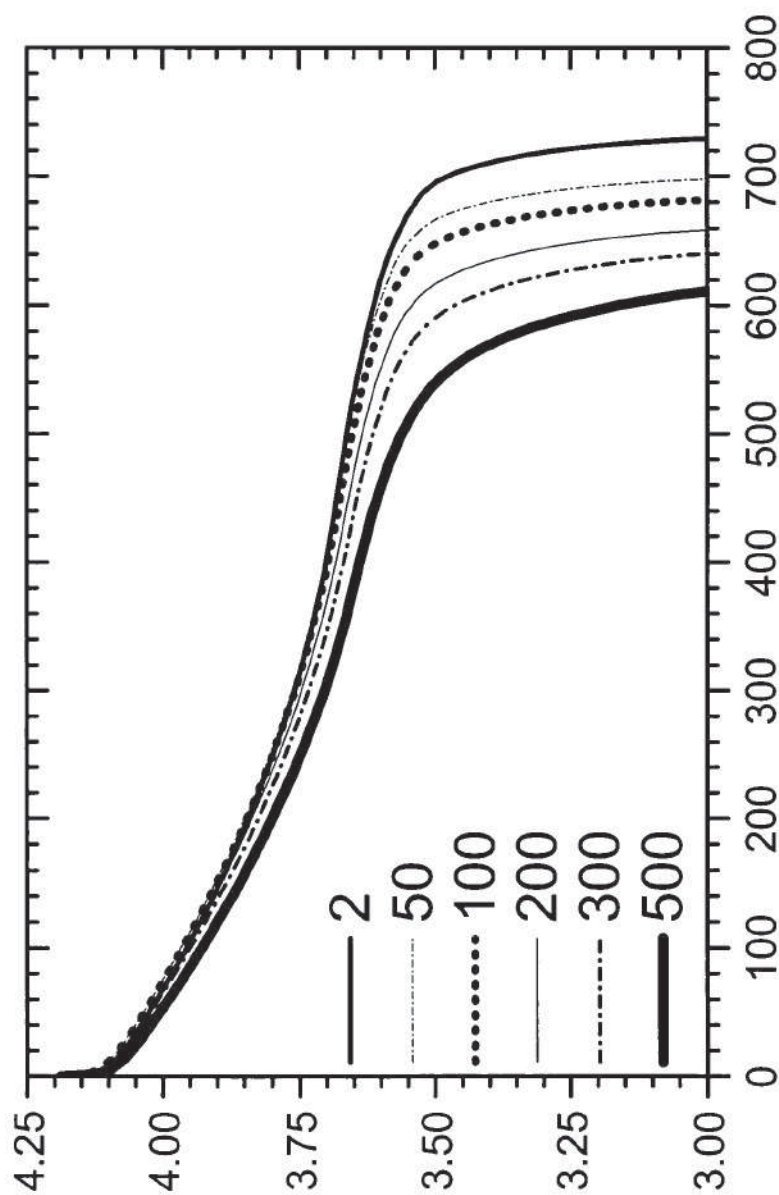


Figure 11a)

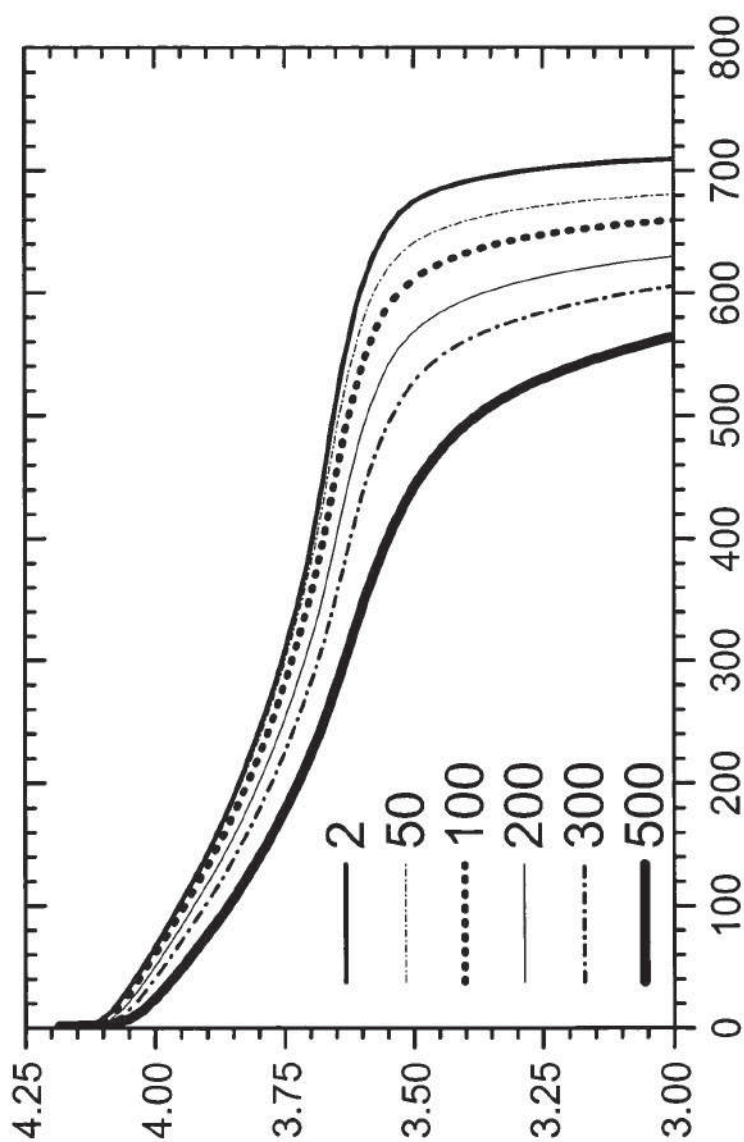


Figure 11b)

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2010/003096

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01G51/00 C01G51/04

ADD.

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)

C01G

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)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2009/074311 A1 (UMICORE [BE]; ELLENWOOD ROBERT [CA]; PAULSEN JENS [KR]) 18 June 2009 (2009-06-18) page 5, line 7 - page 11, line 22 examples 2-5	1-6
A	US 2007/264573 A1 (YAMADA RYOJI [JP] ET AL) 15 November 2007 (2007-11-15) example 5 paragraph [0039] - paragraph [0077] claims 1,2,12,14,15	1-6
A	CN 1 982 219 A (XU WENXIANG [CN]) 20 June 2007 (2007-06-20) * abstract claims 1-3	1-6

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Further documents are listed in the continuation of Box C.



See patent family annex.

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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

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Date of the actual completion of the international search

24 August 2010

Date of mailing of the international search report

31/08/2010

Name and mailing address of the ISA/

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Marino, Emanuela

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/003096

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 101 279 771 A (JINCHUAN GROUP LTD [CN]) 8 October 2008 (2008-10-08) * abstract claims 1-5 examples 1-4	1-6
A	WO 2009/003573 A1 (UMICORE [BE]; CHEN ZHAOHUI [CA]; ELLENWOOD ROBERT [CA]) 8 January 2009 (2009-01-08) cited in the application example 4 page 4, line 22 - page 7, line 25	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2010/003096

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