

METHOD FOR MANUFACTURING DENSE LAYERS THAT CAN BE USED AS ELECTRODES AND/OR ELECTROLYTES FOR LITHIUM ION BATTERIES, AND LITHIUM ION MICROBATTERIES OBTAINED IN THIS WAY

Technical field of the invention

- 5 The present invention relates to the manufacture of dense layers, suitable for use in electrochemical devices, particularly as a layer of electrodes or electrolytes. These layers can be used particularly in multiplayer batteries, such as lithium ion microbatteries. They are manufactured from inorganic nanoparticles, which can optionally have received a functionalisation with a layer of organic coating, which can be polymeric.
- 10 The invention also relates to a novel method for manufacturing these dense layers from nanoparticles. It also relates to the layers obtained with this method, and the multilayer microbatteries incorporating at least one layer obtained with this method.

The invention also relates to a novel method for manufacturing lithium ion batteries, wherein at least one dense electrode layer is deposited using the novel method for
15 manufacturing dense layers, and wherein a porous layer is also deposited.

Prior art

Lithium ion batteries have the best energy density of the different electrochemical electrical energy storage technologies proposed. There are different architectures and
20 chemical compositions of electrodes for producing lithium ion batteries. The methods for manufacturing lithium ion batteries are described in numerous articles and patents, and the publication "*Advances in Lithium-Ion Batteries*" (ed. W. van Schalkwijk and B. Scrosati), published 2002 (Kluwer Academic / Plenum Publishers) gives a good overview.

There is a growing need for microbatteries, i.e. for rechargeable batteries of very small
25 size, capable of being integrated on electronic cards; these electronic circuits can be used in numerous fields, for example in cards to secure transactions, in electronic tags, in implantable medical devices, in various micromechanical systems.

According to the prior art, lithium ion battery electrodes can be manufactured using coating techniques (particularly: roll coating, doctor blade coating, tape casting, slot-
30 die coating). With these methods, the active materials serving to produce the electrodes are in the form of powders wherein the mean particle size is situated between 5 and 15 μm in diameter. These particles are incorporated in an ink which is formed from these particles and deposited on the surface of a substrate.

These techniques make it possible to produce layers of a thickness between about 50 μm and about 400 μm . According to the thickness of the layers, the porosity thereof and the size of the active particles, the power and the energy of the battery can be modulated. To produce microbatteries, it would be sought to have a smaller thickness.

- 5 The inks (or pastes) deposited to form the electrodes contain active material particles, but also binders (organic), carbon powder for providing electrical contact between particles, and solvents which are evaporated during the electrode drying step. To improve the quality of the electrical contacts between the particles and to compact the deposited layers, a calendaring step is performed on the electrodes. After this compression step, the
10 active particles of the electrodes occupy about 60% of the deposition volume, which means that 40% porosities generally remain between the particles.

The contact between each of the particles is essentially in point form and the structure of the electrode is porous. The porosities are filled with an electrolyte, which can be liquid (aprotic solvent wherein a lithium salt is dissolved) or in the form of more or less
15 polymerised gel impregnated with a lithium salt. The thickness of lithium ion battery electrodes being generally between 50 μm and 400 μm , the lithium ions are transported in the thickness of the electrode via the porosities which are filled with electrolyte (containing lithium salts). According to the quantity and size of the porosities, the diffusion rate of lithium in the thickness of the electrode varies.

- 20 To ensure proper operation of the battery, the lithium ions must diffuse both in the thickness of the particle and in the thickness of the electrode. The diffusion in the particle of active material is slower than in the electrolyte with which the porous electrode is impregnated: this electrolyte is liquid or gelled. The slow diffusion in the electrode particles contributes to the serial resistance of the battery. Also, to achieve a satisfactory battery
25 power, the particle size must be reduced; in standard lithium ion batteries, it is situated typically between 5 μm and 15 μm .

Moreover, according to the thickness of the layers, the size and density of active particles contained in the ink, the power and the energy of the battery can be modulated. The energy density is necessarily increased to the detriment of the power density. High-power
30 battery cells must use electrodes and separators of small thickness and high porosity, whereas increasing the energy density requires, on the other hand, an increase in these same thicknesses and a reduction in the porosity rate. The article "*Optimization of Porosity and Thickness of a Battery Electrode by Means of a Reaction-Zone Model*" by John Newman, published in J. Electrochem. Soc., Vol. 142, No.1 in January 1995,

demonstrates the respective effects of the thicknesses of the electrodes and the porosity thereof on the discharge rate (power) and energy density thereof.

However, increasing the porosity in the electrodes tends to degrade the energy density of the battery: to increase the energy density of the electrodes, it is necessary to reduce the porosity. In current lithium ion batteries, it is essentially the porosities filled with electrolyte situated between the active particles which make it possible to diffuse the lithium ions in the electrode. In the absence of porosities filled with electrolyte, the lithium ions are transported from one particle to the other at the contacts between the particles, this contact being substantially in point form. Thus, the lithium ion transport resistance is such that the battery cannot function.

Furthermore, to function properly, the porosities of the electrodes must be filled with electrolyte. This filling is only possible if these porosities are open. Furthermore, according to the size of the porosities and the tortuosity thereof, impregnating the electrode with the electrolyte can become very difficult, or even impossible. When the porosity rate, impregnated with electrolyte, decreases, the electrical resistance of the layer decreases and the ionic resistance thereof increases. When the porosity falls below 30% or even 20%, the ionic resistance increases significantly as some porosities are then capable of closing again, which prevents the wetting of the electrode by the electrolyte.

Consequently, once it is sought to produce electrode films with no porosities to increase the energy density, it is necessary to limit the thickness of these films to less than 50 μm , and preferably less than 25 μm , in order to enable the rapid diffusion of the lithium ions in the solid, with no loss of power.

To produce dense films, the main process used consists of depositing by means of a vacuum method a film of lithium insertion electrode material. This technique makes it possible to obtain dense films, without porosities, or binders, and having accordingly excellent energy densities, and a satisfactory temperature behaviour.

The absence of porosities makes it possible to transport the lithium ions by diffusion through the film, without having to use organic electrolytes based on polymers or solvent containing lithium salts.

Such completely inorganic films provide excellent performances in terms of ageing, safety and temperature behaviour.

PVD (Physical Vapour Deposition) is the currently the most commonly used technology for manufacturing microbatteries in thin layers. Indeed, these products requires films free

from porosities and other point defects to ensure a low electrical resistivity, and the proper ionic conduction required for the proper operation of the electrochemical devices.

The deposition rate obtained with such technologies is of the order of 0.1 μm to 1 μm per hour. PVD deposition techniques make it possible to obtain films of very high quality, containing virtually no point defects, and make it possible to carry out depositions at relatively low temperatures. However, due to the difference in evaporation rate between the different elements, it is difficult to deposit complex compounds with such techniques, and control the stoichiometry of the layer. This technique is perfectly suitable for producing thin layers of simple chemical composition, but once it is sought to increase the deposition thickness the deposition time becomes too great to envisage industrial use in the field of low-cost products.

Furthermore, the vacuum deposition techniques used to produce such films are very costly and difficult to implement industrially on large surface areas, with a high productivity.

The other technologies currently available to produce dense ceramic films, comprise embodiments based on the densification of compact particle depositions or indeed obtaining film using sol-gel type techniques. Sol-gel techniques consist of depositing on the surface of a substrate a polymeric lattice obtained after hydrolysis, polymerisation and condensation steps. The sol-gel transition occurs during the evaporation of the solvent which accelerates the reaction processes on the surface. This technique makes it possible to produce very thin compact depositions. The films thus obtained have a thickness of the order of about one hundred nanometres. These thicknesses are then too small to enable reasonable energy storage in battery applications.

To increase the deposition thickness without giving rise to the risk of onset of cracks or crazing, it is necessary to proceed with successive steps. However, this lowers the industrial productivity of this technique, once it is sought to increase the thickness of the layers.

It is also possible to produce ceramic electrode and/or electrolyte films for batteries by powder sintering. For this, a paste containing ceramic particles and organic binders are placed in film form to obtain a precursor strip commonly known as "green-sheet".

This precursor strip is then calcined to remove the organic matter and sintered at a high temperature to obtain a sheet of ceramic material.

In this case, the metallic films serving to collect current on these electrodes are also deposited using inking techniques. The metallic powders will also be sintered at the same

time as the "green-sheet". Indeed, during the sintering step, the porosities between the particles of ceramic material will be filled, which will result in a shrinking of the strip.

Sintering the current collectors with the ceramic films makes it possible to accommodate the dimensional variations of the ceramic films and metallic collectors and prevent the onset of cracks.

These methods operate at very high temperatures. However, battery materials are generally temperature-sensitive and are rapidly degraded when subjected to such heat treatments.

In order to lower this sintering temperature, the use of nanoparticles has been proposed. In this case, it consists of producing compact depositions of non-agglomerated nanoparticles. These depositions can be readily sintered at relatively low temperatures. This low temperature makes it possible to envisage carrying out sintering directly on metallic substrates.

However, it is observed that these depositions, when they are produced on metallic substrates, are conducive, depending on the thickness of the deposition, the compactness thereof, the particle size, to the onset of cracks during the drying and/or sintering steps.

Electrophoretic nanoparticle deposition techniques have been used to increase the compactness of the depositions and thus facilitate low-temperature sintering with fewer cracks; this is described in several patent applications, for example WO 2013/064 773, WO 2013/064 776, WO 2013/064 777 and WO 2013/064 779 (Fabien Gaben). Thermal coalescence is carried out at a temperature which is especially low as the nanoparticle size is small, and in practice preferably less than 100 nm.

The present invention seeks to remedy at least in part the drawbacks of the prior art mentioned above.

More specifically, the problem addressed by the present invention is that of providing a method for manufacturing dense ceramic layers, directly on a metallic substrate, which is simple, safe, quick, easy to implement, inexpensive.

The aim of the present invention is also that of producing dense solid (ceramic) layers, suitable for lithium ion microbatteries, containing no or very few defects and porosity.

The aim of the present invention is also that of providing dense electrodes and dense electrolytes having a high ionic conductivity, a stable mechanical structure, a good thermal stability and a long service life.

A further aim of the invention is that of providing a method for manufacturing an electronic, electrical or electrotechnical device such as a microbattery, a capacitor, a supercapacitor, a photovoltaic cell comprising a dense electrode or a dense electrolyte according to the invention.

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Subject matter of the invention

According to the invention, the problem is solved by a method for manufacturing a dense layer, comprising the steps of:

- supplying a substrate and a suspension of non-agglomerated nanoparticles of a material P,
- depositing a layer, on said substrate, using the suspension of primary nanoparticles of a material P;
- drying the layer thus obtained,
- densifying the dried layer by mechanical compression and/or heat treatment,

15 knowing that the drying step and the densification step can be performed at least partially at the same time, or during a temperature ramp.

Said method, which forms a first aim of the present invention, is characterised in that the suspension of non-agglomerated nanoparticles of material P comprises nanoparticles of material P having a specific size distribution, making it possible to obtain a density greater than 75% after deposition. Said size is characterised by the D_{50} value thereof.

20 This particle size distribution can be obtained either:

- continuously: In this case, the ratio of standard deviation/mean size of the nanoparticles of material P must be greater than 0.6, and the mean size of the primary nanoparticles of material P less than or equal to 50 nm; or
- discontinuously: in this case, the size distribution of the nanoparticles of material P comprises nanoparticles of a first size D1 between 50 nm and 20 nm, and nanoparticles of a second size D2 at least five times less than that of D1. Very advantageously, the particles of size D1 represent between 50 and 75% of the total mass of nanoparticles.

30 Said suspension of non-agglomerated nanoparticles of material P can be obtained using a monodisperse suspension of size D1, and/or said suspension of nanoparticles of size D2 can be obtained using a monodisperse suspension.

According to the invention, the deposition of the solid and dense ceramic layer is performed electrophoretically, by the dip-coating method, by the ink jet printing method, by roll coating, by slot-die coating, by curtain coating, or by doctor blade coating.

5 After deposition, the dried layer has a density greater than 75%, thanks to the particle size distribution of the constituent nanoparticles thereof. This density can be increased further by a step of densifying the dried layer, by mechanical compression and/or by a heat treatment.

A second aim of the invention is a dense layer capable of being obtained by the method according to the first aim. It can particularly be selected from an anode, a cathode and/or
10 an electrolyte for a lithium ion battery.

A third aim of the invention is a dense layer in an electrochemical, electronic, electrical or electrotechnical device, such as a battery (and preferably a lithium ion battery), a capacitor, a supercapacitor, a capacitance, a resistor, an induction coil, a transistor, said dense layer being capable of being obtained with the method according to the invention.
15 Said dense layer can particularly be an anode layer, a cathode layer and/or an electrolyte layer.

A fourth aim of the invention is a method for manufacturing a dense layer in a lithium ion battery, said method having the features of the method for manufacturing a dense layer stated above, wherein all the embodiments can be implemented for manufacturing a
20 dense layer in a lithium ion battery.

A final aim of the invention is an electrochemical device, and particularly a microbattery, and in particular a lithium ion microbattery, comprising at least one dense layer according to the second aim of the invention.

In an embodiment, said lithium ion microbattery comprises an anode and a cathode which
25 are dense layers according to the invention. This anode and/or this cathode can have a thickness between about 1 μm and about 50 μm .

In a first variant, the electrolyte layer thereof can also be a dense layer according to the invention. In a second variant, said microbattery comprises a liquid electrolyte infiltrated in a porous separator separating said anode and said cathode. This electrolyte layer or this
30 separator has advantageously a thickness between about 1 μm and about 20 μm , and preferably between about 3 μm and about 10 μm .

In a further embodiment, only the electrolyte layer thereof is a dense layer according to the invention.

Detailed description

1. Definitions

Within the scope of the present document, the size of a particle is defined by the greatest dimension thereof. The term "nanoparticle" denotes any particle or object of nanometric size having at least one of the dimensions thereof less than or equal to 100 nm. This size D is expressed here as the size D_{50} .

The term "nanoparticle" is used here to denote primary particles, as opposed to particles formed by aggregation or agglomeration of several primary particles. Such agglomerates can be reduced to nanoparticles (in the sense understood here) by a dispersion operation, for example by grinding or ultrasonic treatment.

The density of a layer is expressed here as a relative value (for example in percent), which is obtained by comparing between the actual density of the layer (designated here as d_{layer}) and the theoretical density of the constituent solid material (designated here as $d_{\text{theoretical}}$). Thus, the porosity of the layer, expressed in percent, is determined as follows:

$$\text{Porosity [\%]} = [(d_{\text{theoretical}} - d_{\text{layer}})/d_{\text{theoretical}}] \times 100.$$

Within the scope of the present document, an electronically insulating material or layer, preferably an ionic conductive layer is a material or a layer wherein the electrical resistivity (resistance to electron flow) is greater than $10^5 \Omega \cdot \text{cm}$. The term "ionic liquid" denotes any liquid salt, capable of transporting electricity, differentiated from all molten salts by a melting point less than 100°C . Some of these salts remain liquid at ambient temperature and do not solidify, even at very low temperatures. Such salts are referred to as "ionic liquids at room temperature".

The term "mesoporous" materials denotes any solid which has within the structure thereof so-called "mesopores" having an intermediate size between that of micropores (width less than 2 nm) and that of macropores (width greater than 50 nm), namely a size between 2 nm and 50 nm. This terminology matches that adopted by IUPAC (International Union for Pure and Applied Chemistry), which is the reference for a person skilled in the art. Therefore, the term "nanopore" is not used here, even though mesopores as defined above have nanometric dimensions according to the definition of nanoparticles, knowing that pores of a size less than that of mesopores are referred to by a person skilled in the art as "micropores".

An overview of the concepts of porosity (and of the terminology set out above) is given in the article "*Texture des matériaux pulvérulents ou poreux*" by F. Rouquerol et al., published in the "*Techniques de l'Ingénieur*" collection, Analysis and Characterisation paper, section P 1050; this article also describes porosity characterisation techniques, particularly the BET method.

According to the present invention, the term "mesoporous layer" denotes a layer which has mesopores. As will be explained below, in these layers, the mesopores contribute significantly to the total porous volume; this fact is conveyed by the expression "Mesoporous layer of porosity greater than X% by volume" used in the description below where X% is preferably greater than 25%, more preferably greater than 30% and even more preferably between 30 and 50% of the total volume of the layer.

The term "aggregate" denotes, according to the IUPAC definitions, a weakly bonded assemblage of primary particles. In this case, these primary particles are nanoparticles having a diameter which can be determined by transmission electron microscopy. An aggregate of aggregated primary nanoparticles can normally be destroyed (i.e. reduced to primary nanoparticles) suspended in a liquid phase under the effect of ultrasound, according to a technique known to a person skilled in the art.

The term "agglomerate" denotes, according to the IUPAC definitions, a strongly bonded assemblage of primary particles or aggregates.

According to the present invention, the term "electrolyte layer" relates to the layer inside an electrochemical device, this device being capable of operating according to its end use. The electrolyte layer is an ionic conductor, but it is electronically insulating. By way of example, in the case where the electrochemical device is a secondary lithium ion battery, the term "electrolyte layer" denotes, either the dense electrolyte layer wherein lithium cations move, or a "porous inorganic layer" impregnated with a phase carrying lithium ions. Said porous inorganic layer in an electrochemical device is here also referred to as "separator", according to the terminology used by a person skilled in the art.

2. Detailed description

According to the invention, the problem is solved by a method for depositing a layer using a nanoparticle suspension, wherein the size of the nanoparticles has a particle size distribution of a particular type.

According to one of the essential aspects of the invention, a nanoparticle suspension is used which represents a particular nanoparticle size distribution, in such a way as to significantly increase the density of the deposition of nanoparticles before sintering.

Obtaining the most compact deposition possible before sintering will make it possible to
5 reduce the shrinking and the risk of cracking. In order to obtain the most compact deposition possible, it is not only necessary to perfectly control the nanoparticle size distribution but also to have the most compact deposition possible of these nanoparticles, without agglomeration.

To obtain such compact depositions, it is possible to either use electrophoretic deposition
10 techniques of dilute suspensions, or indeed deposition techniques of non-agglomerated concentrated suspensions of these polydisperse nanoparticles, by inking, dip-coating, curtain coating, doctor blade, slot-die, etc. Obtaining such concentrated suspensions requires the use of stabilisers, which are organic ligands (for example of PVP type), in order to prevent agglomeration phenomena between nanoparticles. These ligands will be
15 removed at the start of the sintering heat treatment: typically, an intermediate thermal ramp is completed in order to remove all these organic compounds before sintering.

The viscosity of the suspension used for deposition is essentially dependent on the nature of the liquid phase (solvent), the size of the particles and the concentration thereof (expressed by the dry extract). The viscosity of the suspension, as well as the parameters
20 of the deposition method (particularly the travel speed or the passage speed in the liquid) determine the thickness of the deposition. According to these parameters inherent to the deposition technique, the viscosity generally used for dip coating, curtain coating or slot-die coating can vary widely and is situated between about 20 cP and about 2000 cP, measured at 20°C. A colloidal suspension intended to carry out a deposition is frequently
25 referred to as an "ink", regardless of the viscosity thereof.

Once these organic compounds have been removed, the nanoparticles will come into contact and commence the consolidation process. The surfaces of the nanoparticles will weld together at the contact points; this phenomenon is known as "necking" (neck formation). During sintering, these contact points which have become welding zones will
30 increase by diffusion, until they fill the voids left by the initial porosity of the deposition. The filling of these voids is the cause of the shrinking.

In addition, to obtain a final porosity rate less than 15%, preferably less than 10%, on the thick depositions produced on metallic substrates with no cracks, it is necessary to maximise the compactness of the initial nanoparticle deposition, while retaining the

nanometric effect which makes it possible to reduce the consolidation temperatures and keep them compatible with the use of metallic substrates.

According to the invention, colloidal nanoparticle suspensions are used wherein the mean nanoparticle size does not exceed 100 nm. These nanoparticles have moreover a
5 relatively broad size distribution. When this size distribution observes an approximately Gaussian distribution, then the ratio (σ/R_{mean}) of the standard deviation over the mean radius of the nanoparticles must be greater than 0.6.

To increase this compactness of the initial deposition before sintering, it is also possible to use a mixture of two nanoparticle size populations. In this case, the mean diameter of the
10 greatest distribution should not exceed 100 nm, and preferably not exceed 50 nm. This first population of the largest nanoparticles may have a narrower size distribution with a σ/R_{mean} ratio less than 0.6. This population of "large" nanoparticles should represent between 50% and 75% of the dry extract of the deposition (expressed as a mass percentage with respect to the total mass of nanoparticles in the deposition). The second
15 population of nanoparticles will consequently represent between 50% and 25% of the dry extract of the deposition (expressed as a mass percentage with respect to the total mass of nanoparticles in the deposition). The mean diameter of the particles of this second population should be at least 5 times smaller than that of the largest nanoparticle population. As for the largest nanoparticles, the size distribution of this second population
20 may be narrower and with potentially a σ/R_{mean} ratio less than 0.6. It is preferred that the mean diameter of the second population is at least one fifteenth of the largest nanoparticle population, and preferably at least one twelfth; this facilitates the densification of the layer after the deposition thereof.

In any case, the two populations should show agglomeration in the ink produced. In
25 addition, these nanoparticles can be advantageously synthesised in the presence of ligands or organic stabilisers so as to prevent aggregation or agglomeration of the nanoparticles.

The preparation of colloidal suspensions by wet nanogrinding makes it possible to obtain relatively broad size distributions. However, according to the nature of the ground
30 material, the "fragility" thereof, the reduction factor applied, the primary nanoparticles can be damaged or amorphised.

The materials used in manufacturing lithium ion batteries are particularly sensitive, the slightest modification of the crystalline state thereof or of the chemical composition thereof results in degraded electrochemical performances. In addition, for this type of application,

it is preferable to use nanoparticles prepared in suspension directly by precipitation, according to solvothermal or hydrothermal type methods, at the desired primary nanoparticle size.

These methods for synthesising nanoparticles by precipitation make it possible to obtain
5 primary nanoparticles of homogeneous size with a reduced size distribution, of good crystallinity and purity. It is also possible to obtain with these methods very small particle sizes, potentially less than 10 nm, and in a non-aggregated state. For this, it is necessary to add a ligand directly into the synthesis reactor so as to prevent the formation of agglomerates, aggregates during synthesis. For example, PVP can be used to perform
10 this function.

As the non-agglomerated nanoparticle size distribution obtained by precipitation is relatively narrow, it is necessary to prefer a colloidal suspension preparation strategy mixing two size distributions following the rules described above in order to maximise the compactness of the deposition before sintering. This will make it possible after sintering to
15 produce relatively thick depositions, directly on metallic substrates with little or no risks of cracking during the sintering heat treatment which will be maintained at a relatively low temperature due to the small size of the nanoparticles used.

The bimodal nanoparticle suspension is then used to deposit the compact layers, which will then be densified by a low-temperature heat treatment and suitable for use particularly
20 as electrodes or electrolyte in electrochemical devices such as for example lithium ion batteries. Various methods can be used for depositing these layers, particularly electrophoresis, a printing method selected from ink-jet printing and flexographic printing, and a coating method selected preferably from doctor blade coating, roll coating, curtain coating, dip-coating, slot-die coating. These methods are simple, safe, easy to implement,
25 industrialise, and make it possible to obtain a homogeneous final dense layer. Electrophoresis makes it possible to deposit a uniform layer on large surface areas with a high deposition speed. Coating techniques, particularly dip-coating, roll coating, curtain coating or doctor blade coating, make it possible to simplify the management of baths with respect to electrophoresis, as the composition of the bath remains constant during
30 deposition by coating. Ink-jet printing deposition makes it possible to produce localised depositions.

Dense electrodes and electrolytes in a thick layer and produced in a single step can be obtained with the methods cited above using bimodal or polydisperse nanoparticle suspensions.

The method according to the invention makes it possible to manufacture dense layers having a density of at least 90% of the theoretical density, preferably at least 95% of the theoretical density, and even more preferably at least 96% of the theoretical density, and optimally at least 97% of the theoretical density, knowing that the remainder consists of a residual porosity, which consists of closed pores.

The embodiment of a dense electrode according to the invention is now described by way of non-limiting example; in this description, a more in-depth description of certain details of the method according to the invention is given.

Nature of the current collector

As a general rule, the substrate serving as a current collector in the batteries using dense electrodes according to the invention is metallic, for example a metal sheet. It must be selected so as to withstand the temperature of any heat or thermomechanical treatment which will be applied on the layer deposited on this substrate, and this temperature will be dependent on the chemical nature of said layer. The substrate is preferably selected from strips made of titanium, molybdenum, chromium, tungsten, copper, nickel or stainless steel or any alloy containing at least one of the preceding elements.

As a general rule, the metal sheet can be coated with a layer of noble metal, particularly selected from gold, platinum, palladium, titanium, molybdenum, tungsten, chromium or alloys containing mostly at least one or more of these metals, or a layer of ITO type conductive material (which has the advantage of also acting as a diffusion barrier).

In this example, we will use a sheet of 316L type stainless steel of 10 microns in thickness.

Deposition of a dense electrode layer by dip-coating

As a general rule, this electrode layer can be deposited either on a metallic surface of the current collector, or on another dense or porous inorganic layer, for example on a dense electrolyte layer or on a porous separator.

It is possible to deposit bimodal nanoparticles with the dip-coating method, regardless of the chemical nature of the nanoparticles used; obviously, the other deposition techniques mentioned above can also be used.

For example, to produce a dense ceramic deposition of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, we can produce an ink composed of nanoparticles of two different sizes, in the case of anode made of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, nanoparticles of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ of about 5 nm are synthesised by the glycothermal route (see

the article "*Impact of the Synthesis Parameters on the microstructure of nano-structured LTO prepared by glycothermal routes and ^7Li NMR structural investigations*", M. Odziomek, F. Chaput et al., published in J Sol-Gel Sci Technol 89, 225–233 (2019)). To this synthesis, ligands are added to limit nanoparticle agglomeration. These nanoparticles of 5 nm in diameter are associated with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles obtained by hydrothermal synthesis with particle sizes of 30 nm.

These nanoparticles are mixed, dispersed by ultrasound, with 70% by mass of 30 nm particles and 30% by mass of 5 nm nanoparticles in an ink with 15% overall dry extract, in ethanol and containing PVP as a stabiliser. Each dip-coating pass only produces a layer of relatively limited thickness; the wet layer must be dried. In order to obtain a layer of a desired final thickness, the dip-coating deposition step followed by the step of drying the layer can be repeated as many times as required.

Although this succession of dip-coating/drying steps is time-consuming, the dip-coating deposition method is a method that is simple, safe, easy to implement, industrialise and making it possible to obtain a homogeneous and compact final layer.

Treatment and properties of the deposited layers

As a general rule, the layers deposited by dip-coating must be dried. Once dried, a heat treatment is performed in two phases. In a first phase, the deposition is maintained for 10 minutes at 400°C in order to calcine all the organic compounds contained therein. Then the treatment temperature is increased to 550°C and maintained for one hour at this temperature in order to obtain the consolidation of the deposition.

The selection of the materials of the nanoparticles is obviously dependent on the function of the layers thus deposited in the targeted electrochemical, electrical or electronic device. As a general rule, the nanoparticles used in the present invention are inorganic and non-metallic, knowing that they can be coated with an organic functionalisation layer ("core-shell" type particles); this will be described hereinafter. These particles coated with an organic layer are included here in the term "inorganic particles".

If the layer according to the invention is to function as a cathode of a battery, particularly a lithium ion battery, it can be produced for example from a material P which a cathode material selected from:

- the oxides LiMn_2O_4 , $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ where $0 < x < 0.15$, LiCoO_2 , LiNiO_2 , $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, $\text{LiMn}_{1.5}\text{Ni}_{0.5-x}\text{X}_x\text{O}_4$ where X is selected from Al, Fe, Cr, Co, Rh, Nd, other rare earths such as Sc, Y, Lu, La, Ce, Pr, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and where $0 < x < 0.1$, $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ where M = Er, Dy, Gd, Tb, Yb, Al, Y, Ni, Co, Ti, Sn, As, Mg or a mixture of these compounds and where $0 < x < 0.4$, LiFeO_2 , $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ where $0 \leq x < 0.15$, $\text{LiNi}_{1/x}\text{Co}_{1/y}\text{Mn}_{1/z}\text{O}_2$ where $x+y+z=10$;
- the phosphates LiFePO_4 , LiMnPO_4 , LiCoPO_4 , LiNiPO_4 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; the phosphates of formula $\text{LiMM}'\text{PO}_4$, where M and M' ($M \neq M'$) are selected from Fe, Mn, Ni, Co, V;
- all lithiated forms of the following chalcogenides: V_2O_5 , V_3O_8 , TiS_2 , titanium oxysulphides (TiO_yS_z where $z=2-y$ and $0.3 \leq y \leq 1$), tungsten oxysulphides (WO_yS_z where $0.6 < y < 3$ and $0.1 < z < 2$), CuS , CuS_2 , preferably $\text{Li}_x\text{V}_2\text{O}_5$ where $0 < x \leq 2$, $\text{Li}_x\text{V}_3\text{O}_8$ where $0 < x \leq 1.7$, Li_xTiS_2 where $0 < x \leq 1$, titanium and lithium oxysulphides $\text{Li}_x\text{TiO}_y\text{S}_z$ where $z = 2-y$, $0.3 \leq y \leq 1$, $\text{Li}_x\text{WO}_y\text{S}_z$, Li_xCuS , Li_xCuS_2 .

If the layer according to the invention is to function as an anode of a battery, particularly a lithium ion battery, it can be produced for example from a material P which an anode material selected from:

- carbon nanotubes, graphene, graphite;
- lithiated iron phosphate (of typical formula LiFePO_4);
- mixed silicon and tin oxynitrides (of typical formula $\text{Si}_a\text{Sn}_b\text{O}_y\text{N}_z$ where $a>0$, $b>0$, $a+b \leq 2$, $0 < y \leq 4$, $0 < z \leq 3$) (also known as SiTON), and in particular $\text{SiSn}_{0.87}\text{O}_{1.2}\text{N}_{1.72}$; as well as oxynitrides-carbides of typical formula $\text{Si}_a\text{Sn}_b\text{C}_c\text{O}_y\text{N}_z$ where $a > 0$, $b > 0$, $a+b \leq 2$, $0 < c < 10$, $0 < y < 24$, $0 < z < 17$;
- nitrides of type Si_xN_y (in particular where $x=3$ and $y=4$), Sn_xN_y (in particular where $x=3$ and $y=4$), Zn_xN_y (in particular where $x=3$ and $y=2$), $\text{Li}_{3-x}\text{M}_x\text{N}$ (where $0 \leq x \leq 0.5$ for $M=\text{Co}$, $0 \leq x \leq 0.6$ for $M=\text{Ni}$, $0 \leq x \leq 0.3$ for $M=\text{Cu}$); $\text{Si}_{3-x}\text{M}_x\text{N}_4$ where $M=\text{Co}$ or Fe and $0 \leq x \leq 3$.
- the oxides SnO_2 , SnO , Li_2SnO_3 , SnSiO_3 , Li_xSiO_y ($x \geq 0$ and $2 > y > 0$), $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiNb_2O_7 , Co_3O_4 , $\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ and TiO_2 ,
- composite oxides TiNb_2O_7 comprising between 0% and 10% by mass of carbon, preferably the carbon being selected from graphene and carbon nanotubes,
- compounds of general formula $\text{Li}_w\text{Ti}_{1-x}\text{M}^1_x\text{Nb}_{2-y}\text{M}^2_y\text{O}_{7-z}\text{M}^3_z$ wherein M^1 and M^2 are each at least one elements selected in the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs and Sn, M^3

and M^2 optionally being identical or different from one another, and wherein M^3 is at least one halogen, and wherein $0 \leq w \leq 5$, $0 \leq x < 1$, $0 \leq y < 2$ and $0 < z \leq 0.3$.

If the layer according to the invention is to function as an electrolyte in a battery, particularly a lithium ion battery, it can be produced for example from a material P which is
 5 an electrolyte material selected from:

- garnets of formula $Li_dA^1_xA^2_y(TO_4)_z$ where A^1 represents a cation of degree of oxidation +II, preferably Ca, Mg, Sr, Ba, Fe, Mn, Zn, Y, Gd; and where A^2 represents a cation of degree of oxidation +III, preferably Al, Fe, Cr, Ga, Ti, La; and where (TO_4) represents an anion wherein T is an atom of degree of oxidation +IV, located at the centre of a tetrahedron formed by oxygen atoms, and wherein TO_4 represents advantageously the silicate or zirconate anion, knowing that all or part of the elements T of a degree of oxidation +IV can be replaced by atoms of a degree of oxidation +III or +V, such as Al, Fe, As, V, Nb, In, Ta; knowing that: d is between 2 and 10, preferably between 3 and 9, and even more preferably between 4 and 8; x is between 2.6 and 3.4 (preferably between 2.8 and 3.2); y is between 1.7 and 2.3 (preferably between 1.9 and 2.1) and z is between 2.9 and 3.1;
- garnets, preferably selected from: $Li_7La_3Zr_2O_{12}$; $Li_6La_2BaTa_2O_{12}$; $Li_{5.5}La_3Nb_{1.75}In_{0.25}O_{12}$; $Li_5La_3M_2O_{12}$ where M = Nb or Ta or a mixture of these two compounds; $Li_{7-x}Ba_xLa_{3-x}M_2O_{12}$ where $0 \leq x \leq 1$ and M = Nb or Ta or a mixture of the two compounds; $Li_{7-x}La_3Zr_{2-x}M_xO_{12}$ where $0 \leq x \leq 2$ and M = Al, Ga or Ta or a mixture of two or three of these compounds;
- lithiated phosphates, preferably selected from: lithiated phosphates of the type NaSICON, Li_3PO_4 ; $LiPO_3$; $Li_3Al_{0.4}Sc_{1.6}(PO_4)_3$ referred to as "LASP"; $Li_{1.2}Zr_{1.9}Ca_{0.1}(PO_4)_3$; $LiZr_2(PO_4)_3$; $Li_{1+3x}Zr_2(P_{1-x}Si_xO_4)_3$ where $1.8 < x < 2.3$; $Li_{1+6x}Zr_2(P_{1-x}B_xO_4)_3$ where $0 \leq x \leq 0.25$; $Li_3(Sc_{2-x}M_x)(PO_4)_3$ where M=Al or Y and $0 \leq x \leq 1$; $Li_{1+x}M_x(Sc)_{2-x}(PO_4)_3$ where M = Al, Y, Ga or a mixture of the three compounds and $0 \leq x \leq 0.8$; $Li_{1+x}M_x(Ga_{1-y}Sc_y)_{2-x}(PO_4)_3$ where $0 \leq x \leq 0.8$; $0 \leq y \leq 1$ and M= Al or Y or a mixture of both compounds; $Li_{1+x}M_x(Ga)_{2-x}(PO_4)_3$ where M = Al, Y or a mixture of both compounds and $0 \leq x \leq 0.8$; $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ where $0 \leq x \leq 1$ referred to as "LATP"; or $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ where $0 \leq x \leq 1$ referred to as "LAGP"; or $Li_{1+x+z}M_x(Ge_{1-y}Ti_y)_{2-x}Si_zP_{3-z}O_{12}$ where $0 \leq x \leq 0.8$ and $0 \leq y \leq 1.0$ and $0 \leq z \leq 0.6$ and M= Al, Ga or Y or a mixture of two or three of these compounds; $Li_{3+y}(Sc_{2-x}M_x)Q_yP_{3-y}O_{12}$ where M = Al and/or Y and Q = Si and/or Se, $0 \leq x \leq 0.8$ and $0 \leq y \leq 1$; or $Li_{1+x+y}M_xSc_{2-x}Q_yP_{3-y}O_{12}$ where M = Al, Y, Ga or a mixture of the three compounds and Q = Si and/or Se, $0 \leq x \leq 0.8$ and $0 \leq y \leq 1$; or

- Li_{1+x+y+z}M_x(Ga_{1-y}Sc_y)_{2-x}Q_zP_{3-z}O₁₂ where 0 ≤ x ≤ 0.8, 0 ≤ y ≤ 1, 0 ≤ z ≤ 0.6 where M = Al or Y or a mixture of both compounds and Q= Si and/or Se; or Li_{1+x}Zr_{2-x}B_x(PO₄)₃ where 0 ≤ x ≤ 0.25; or Li_{1+x}Zr_{2-x}Ca_x(PO₄)₃ where 0 ≤ x ≤ 0.25; or Li_{1+x}M³_xM_{2-x}P₃O₁₂ where 0 ≤ x ≤ 1 and M³= Cr, V, Ca, B, Mg, Bi and/or Mo, M = Sc, Sn, Zr, Hf, Se or Si, or a mixture of these compounds; Li_{1+2x}Ca_xZr_{2-x}(PO₄)₃ where 0 ≤ x ≤ 0.25;
- 5
- lithiated borates, preferably selected from: Li₃(Sc_{2-x}M_x)(BO₃)₃ where M=Al or Y and 0 ≤ x ≤ 1; Li_{1+x}M_x(Sc)_{2-x}(BO₃)₃ where M = Al, Y, Ga or a mixture of the three compounds and 0 ≤ x ≤ 0.8; Li_{1+x}M_x(Ga_{1-y}Sc_y)_{2-x}(BO₃)₃ where 0 ≤ x ≤ 0.8, 0 ≤ y ≤ 1 and M= Al or Y; Li_{1+x}M_x(Ga)_{2-x}(BO₃)₃ where M = Al, Y or a mixture of both
- 10
- compounds and 0 ≤ x ≤ 0.8; Li₃BO₃, Li₃BO₃-Li₂SO₄, Li₃BO₃-Li₂SiO₄, Li₃BO₃-Li₂SiO₄-Li₂SO₄;
- oxynitrides, preferably selected from Li₃PO_{4-x}N_{2x/3}, Li₄SiO_{4-x}N_{2x/3}, Li₄GeO_{4-x}N_{2x/3} where 0 < x < 4 or Li₃BO_{3-x}N_{2x/3} where 0 < x < 3;
 - lithiated compounds based on lithium and phosphorus oxynitride, referred to as
- 15
- "LiPON", in the form of Li_xPO_yN_z where x ~ 2.8 and 2y+3z ~ 7.8 and 0.16 ≤ z ≤ 0.4, and in particular Li_{2.9}PO_{3.3}N_{0.46}, but also the compounds Li_wPO_xN_yS_z where 2x+3y+2z = 5 = w or the compounds Li_wPO_xN_yS_z where 3.2 ≤ x ≤ 3.8, 0.13 ≤ y ≤ 0.4, 0 ≤ z ≤ 0.2, 2.9 ≤ w ≤ 3.3 or the compounds in the form of Li_tP_xAl_yO_uN_vS_w where 5x+3y=5, 2u+3v+2w=5+t, 2.9≤t≤3.3, 0.84≤x≤0.94, 0.094≤y≤0.26, 3.2≤u≤3.8,
- 20
- 0.13≤v≤0.46, 0≤w≤0.2;
- materials based on lithium phosphorus or boron oxynitrides, referred to respectively as "LiPON" and LIBON", optionally also containing silicon, sulphur, zirconium, aluminium, or a combination of aluminium, boron, sulphur and/or silicon, and boron for materials based on lithium phosphorus oxynitrides;
- 25
- lithiated compounds based on lithium, phosphorus and silicon oxynitride referred to as "LiSiPON", and in particular Li_{1.9}Si_{0.28}P_{1.0}O_{1.1}N_{1.0};
 - lithium oxynitrides of the types LiBON, LiBSO, LiSiPON, LiSON, thio-LiSiCON, LiPONB (where B, P and S represent respectively boron, phosphorus and sulphur);
- 30
- lithium oxynitrides of the type LiBSO such as (1-x)LiBO_{2-x}Li₂SO₄ where 0.4 ≤ x ≤ 0.8;
 - lithiated oxides, preferably selected from Li₇La₃Zr₂O₁₂ or Li_{5+x}La₃(Zr_xA_{2-x})O₁₂ where A = Sc, Y, Al, Ga and 1.4 ≤ x ≤ 2 or Li_{0.35}La_{0.55}TiO₃ or Li_{3x}La_{2/3-x}TiO₃ where 0 ≤ x ≤ 0.16 (LLTO);
- 35
- silicates, preferably selected from Li₂Si₂O₅, Li₂SiO₃, Li₂Si₂O₆, LiAlSiO₄, Li₄SiO₄, LiAlSi₂O₆;

- anti-perovskite type solid electrolytes selected from: Li_3OA where A is a halide or halide mixture, preferably at least one of the elements selected from F, Cl, Br, I or a mixture of two or three or four of these elements; $\text{Li}_{(3-x)}\text{M}_{x/2}\text{OA}$ where $0 < x \leq 3$, M is a divalent metal, preferably at least one of the elements selected from Mg, Ca, Ba, Sr or a mixture of two or three or four of these elements, A is a halide or halide mixture, preferably at least one of the elements selected from F, Cl, Br, I or a mixture of two or three or four of these elements; $\text{Li}_{(3-x)}\text{M}^3_{x/3}\text{OA}$ where $0 \leq x \leq 3$, M^3 is a trivalent metal, A is a halide or a halide mixture, preferably at least one of the elements selected from F, Cl, Br, I or a mixture of two or three or four of these elements; or $\text{LiCOX}_z\text{Y}_{(1-z)}$, where X and Y are halides as mentioned above in relation to A, and $0 \leq z \leq 1$,
- the compounds $\text{La}_{0,51}\text{Li}_{0,34}\text{Ti}_{2,94}$, $\text{Li}_{3,4}\text{V}_{0,4}\text{Ge}_{0,6}\text{O}_4$, $\text{Li}_2\text{O-Nb}_2\text{O}_5$, LiAlGaSPO_4 ;
- formulations based on Li_2CO_3 , B_2O_3 , Li_2O , $\text{Al}(\text{PO}_3)_3\text{LiF}$, P_2S_3 , Li_2S , Li_3N , $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$, $\text{Li}_{3,6}\text{Ge}_{0,6}\text{V}_{0,4}\text{O}_4$, $\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_{3,25}\text{Ge}_{0,25}\text{P}_{0,25}\text{S}_4$, $\text{Li}_{1,3}\text{Al}_{0,3}\text{Ti}_{1,7}(\text{PO}_4)_3$, $\text{Li}_{1+x}\text{Al}_x\text{M}_{2-x}(\text{PO}_4)_3$ (where M = Ge, Ti, and/or Hf, and where $0 < x < 1$), $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (where $0 \leq x \leq 1$ and $0 \leq y \leq 1$).

Use of coated nanoparticles ("core-shell" type)

As a general rule, the nanoparticles used in inks serving to make these depositions intended for electrodes can also have a core-shell structure. Indeed, the performance of the dense electrodes obtained with the method according to the invention will be dependent on the ionic and electronic conduction property thereof. In addition, on the surface of the nanoparticles of active material, it can be important to apply a "shell" of an organic or inorganic material, endowed with good electronic and/or ionic conduction properties.

Thus, in an advantageous embodiment, the core is formed of an electrode material (anode or cathode), and the shell is formed of a material which is both electronically conductive and which does not prevent the passage of lithium ions. By way of example, the shell can be formed by a layer of a metal, which is thin enough to allow lithium ions to pass, or by a layer of graphite thin enough to allow lithium ions to pass, or by an inorganic or organic layer of an ionic conductor which is also a good electronic conductor.

The core-shell approach can also be applied to the manufacture of the electrolyte. Thus, in a further embodiment, the core of the nanoparticles used in the method according to the invention is formed of an electrolyte material, and the shell is formed of an inorganic or organic material which is a good ion conductor, particularly of lithium ions, and which should be a good electronic insulator.

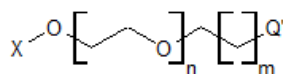
When the shell layer is an organic layer, it is preferred that this layer be made of polymer material. A layer of polymer has, inter alia, the advantage of being malleable, which facilitates the compaction of the layer deposited using these particles.

We now describe a method for preparing inorganic nanoparticles having a polymer shell.

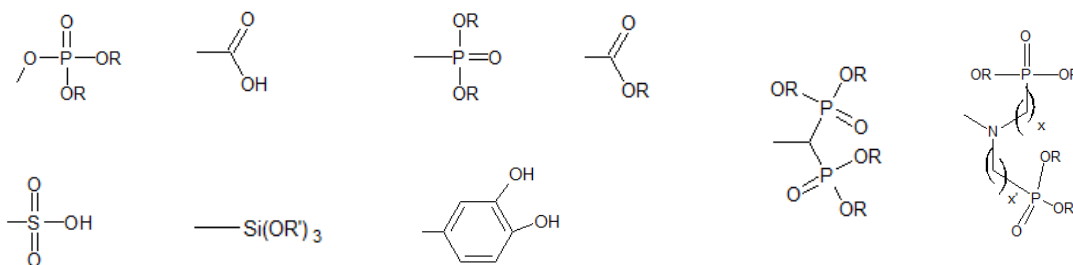
- 5 It is particularly suitable for the nanoparticles of electrolyte material, for which the shell should be an electrical insulator and an ionic conductor. This method, referred to here as "functionalisation" of the inorganic nanoparticles forming the core by a shell, consists of grafting on the surface of the nanoparticles a molecule having a Q- Z type structure wherein Q is a function bonding the molecule to the surface, and Z is preferably a PEO
- 10 group.

By way of Q group, a complexing function of the surface cations of the nanoparticles can be used such as the phosphate or phosphonate function.

Preferably, the inorganic nanoparticles are functionalised by a PEO derivative of the type

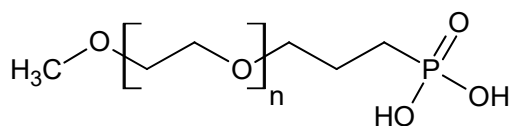


- 15 where X represents an alkyl chain or a hydrogen atom,
n is between 40 and 10,000 (preferably between 50 and 200),
m is between 0 and 10, and
Q' is an embodiment of Q and represents a group selected in the group formed by:



- and where R represents an alkyl chain or a hydrogen atom, R' represents a methyl
- 20 group or an ethyl group, x is between 1 and 5, and x' is between 1 and 5.

More preferably, the inorganic nanoparticles are functionalised by methoxy-PEO-phosphonate



where n is between 40 and 10,000 and preferably between 50 and 200.

According to an advantageous embodiment, a solution of Q-Z (or Q'-Z, where applicable) is added to a colloidal suspension of electrolyte nanoparticles of electrolyte or of electronic insulator so as to obtain a molar ratio between Q (which comprises here Q') and the set of cations present in the inorganic nanoparticles (abbreviated here as "NP-C") between 1 and 0.01, preferably between 0.1 and 0.02. Beyond a molar ratio Q/NP-C of 1, the functionalisation of the electronic inorganic nanoparticles by the molecule Q-Z is liable to induce a steric size such that said nanoparticles cannot be completely functionalised; this is also dependent on the size of the nanoparticles. For a molar ratio Q/NP-C less than 0.01, the molecule Q-Z is liable not to be of a sufficient quantity to provide sufficient conductivity of lithium ions; this is also dependent on the particle size. The use of a greater quantity of Q-Z during functionalisation would result in an unnecessary consumption of Q-Z.

A colloidal suspension of inorganic nanoparticles at a mass concentration between 0.1% and 50%, preferably between 5% and 25%, and even more preferably at 10% is used to carry out the functionalisation of the inorganic nanoparticles. At high concentrations, there can be a risk of bridging and a lack of accessibility of the surface to be functionalised (risk of precipitation or poorly or non-functionalised particles). Preferably, the inorganic nanoparticles are dispersed in a liquid phase such as water or ethanol.

This reaction can be carried out in any suitable solvents capable of solubilising the molecule Q-Z.

According to the molecule Q-Z, the functionalisation conditions can be optimised by adjusting the temperature and duration of the reaction, and the solvent used. After having added a solution of Q-Z to a colloidal suspension of electrolyte nanoparticles, the reaction medium is left under stirring for 0 h to 24 hours (preferably for 5 minutes to 12 hours, and even more preferably for 0.5 hours to 2 hours), such that at least a portion, preferably all of the molecules Q-Z can be grafted on the surface of the inorganic nanoparticles. The functionalisation can be carried out with heating, preferably at a temperature between 20°C and 100°C. The temperature of the reaction medium must be adapted to the choice of the functionalising molecule Q-Z.

These functionalised nanoparticles therefore have a core or inorganic material and a shell of PEO. The thickness of the shell can be typically between 1 nm and 100 nm; this thickness can be determined by transmission electron microscopy after labelling the polymer with ruthenium oxide (RuO_4).

- 5 Advantageously, the nanoparticles thus functionalised are then purified with successive centrifugation cycles and redispersions and/or by tangential filtration.

After redispersing the functionalised inorganic nanoparticles, the suspension can be reconcentrated until the sought dry extract is attained, by any suitable means.

- 10 Advantageously, the dry extract of a suspension of inorganic nanoparticles functionalised with PEO comprises more than 40% (by volume) of solid electrolyte material, preferably more than 60% and even more preferably more than 70% of solid electrolyte material.

The densification of the layer produced with organic core-shell type nanoparticles after the deposition thereof can be carried out by suitable means, preferably:

- 15 a) by any mechanical means, in particular by mechanical compression, preferably uniaxial compression;
- b) by thermocompression, i.e. by heat treatment under pressure. The optimal temperature is closely dependent on the chemical composition of the materials deposited, it is also dependent on the particle sizes and the compactness of the layer. A controlled
- 20 atmosphere is preferably maintained in order to prevent oxidation and surface pollution of the particles deposited.

- 25 Advantageously, the compaction is carried out in a controlled atmosphere and at temperatures between ambient temperature and the melting point of the polymer (typically the PEO) used; the thermocompression can be performed at a temperature between ambient temperature (about 20°C) and about 300°C; but it is preferred not to exceed 200°C (or even more preferably 100°C) in order to prevent PEO degradation.

- 30 As stated above, one of the advantages of organic shells is the malleability of the shell; PEO is for example a readily deformable polymer at a relatively low pressure. Thus, the densification of the nanoparticles of electrolyte or of electronic insulator functionalised by a polymer such as PEO can be obtained solely by mechanical compression (application of a mechanical pressure). Advantageously, the compression is performed in a pressure range between 10 MPa and 500 MPa, preferably between 50 MPa and 200 MPa and at a temperature of the order of 20°C to 200°C.

At the interfaces, PEO is amorphous and ensures good ionic contact between the solid electrolyte particles. PEO can thus conduct lithium ions, even in the absence of liquid electrolyte; PEO is at the same time an electronic insulator. It favours the assembly of the lithium ion battery at low temperatures, thus limiting the risk of interdiffusion at the interfaces between the electrolytes and the electrodes.

In a lithium ion battery, the electrolyte layer obtained after densification can have a thickness less than 10 μm , preferably less than 6 μm , preferably less than 5 μm , in order to limit the thickness and the weight of the battery without diminishing the properties thereof.

10

Use of the method according to the invention for depositing layers in devices which also comprise mesoporous layers

The method according to the invention makes it possible to deposit inorganic dense layers in electrochemical and other devices, such as lithium ion batteries. In these devices, said dense layers can perform the function of an anode or a cathode or an electrode, and the device can include several inorganic dense layers according to the invention. These devices can be of "all-solid-state" type, the dense layers only having a very low porosity. According to a variant of the invention, the device also includes at least one porous inorganic layer.

According to this variant of the invention, the "porous inorganic layer", preferably mesoporous, can be deposited with a method selected preferably in the group formed by: electrophoresis, a printing method, selected preferably from ink-jet printing and flexographic printing, and a coating method selected preferably from roll coating, curtain coating, doctor blade coating, slot-die coating, dip-coating, using a suspension of nanoparticle aggregates or agglomerates, preferably using a concentrated suspension containing nanoparticle agglomerates.

More specifically, a colloidal suspension is used comprising aggregates or agglomerates of nanoparticles of at least one inorganic material, of mean primary diameter D_{50} between 2 nm and 100 nm, preferably between 2 nm and 60 nm, said aggregates or agglomerates typically having a mean diameter D_{50} between 50 nm and 300 nm (preferably between 100 nm and 200 nm). Then the layer thus obtained is dried and the layer is consolidated, by pressing and/or heating, to obtain a porous layer, preferably mesoporous and inorganic. This method is particularly advantageous with nanoparticles formed of electrolyte materials.

The mesoporous layer can be deposited on a dense layer deposited with the method according to the invention, or said dense layer is deposited on said mesoporous layer prepared with the method described above.

5 So that said porous layer can fulfil the electrolyte function thereof, it must be impregnated with a mobile cation carrier liquid; in the case of a lithium ion battery, this cation is a lithium cation. This lithium ion carrier phase is preferably selected in the group formed by:

- o an electrolyte composed of at least one aprotic solvent and at least one lithium salt;
 - o an electrolyte composed of at least one ionic liquid or ionic polyliquid and at least
10 one lithium salt;
 - o a mixture of at least one aprotic solvent and at least one ionic liquid or ionic polyliquid and at least one lithium salt;
 - o a polymer rendered an ionic conductor by adding at least one lithium salt; and
 - o a polymer rendered an ionic conductor by adding a liquid electrolyte, either in the
15 polymer phase, or in the mesoporous structure,
- said polymer being preferably selected in the group formed by poly(ethylene oxide), poly(propylene oxide), polydimethylsiloxane, polyacrylonitrile, poly(methyl methacrylate), poly(vinyl chloride), poly(vinylidene fluoride), PVDF-hexafluoropropylene.

20 Example of manufacture of a lithium ion microbattery

A method for manufacturing lithium ion microbatteries using layers according to the invention is described here.

a) Preparation of the electrodes with the deposition method according to the invention

25 A first dense $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode obtained with the method described above in the section "Deposition of a dense electrode layer by dip-coating" was deposited. A second dense LiMn_2O_4 electrode was also deposited with a similar method.

On each of these two electrodes, a thin mesoporous film of Li_3PO_4 agglomerates, acting as a separating film in the battery, and which was prepared as described hereinafter, was
30 then deposited.

b) Deposition of the separating layer

A suspension of Li_3PO_4 nanoparticles was prepared using the two solutions described hereinafter: Firstly, 45.76 g of CH_3COOLi , $2\text{H}_2\text{O}$ was dissolved in 448 ml of water, then 224 ml of ethanol was added under vigorous stirring to the medium in order to obtain a solution A. Secondly, 16.24 g of H_3PO_4 (85 wt% in water) was diluted in 422.4 ml of water, then 182.4 ml of ethanol was added to this solution in order to obtain a second solution hereinafter referred to as solution B. Solution B was then added, under vigorous stirring, to solution A.

The solution obtained, perfectly clear after the bubbles formed during mixing disappeared, was added to 4.8 litres of acetone under the action of an Ultraturrax™ type homogeniser in order to homogenise the medium. A white precipitation suspended in the liquid phase was immediately observed.

The reaction medium was homogenised for 5 minutes then was kept for 10 minutes under magnetic stirring. The whole was allowed to settle for 1 to 2 hours. The supernatant was removed then the remaining suspension was centrifuged for 10 minutes at 6000 g. Then, 1.2 l of water was added to resuspend the precipitate (use of a sonotrode, magnetic stirring). Two additional washes of this type were then performed with ethanol. Under vigorous stirring, 15 ml of a 1 g/ml Bis(2-(methacryloyloxy)ethyl)phosphate was added to the colloidal suspension in ethanol thus obtained. The suspension thus became more stable. The suspension was then sonicated using a sonotrode. The suspension was then centrifuged for 10 minutes at 6000 g. The pellet was then redispersed in 1.2 l of ethanol then centrifuged for 10 minutes at 6000 g. The pellets thus obtained are redispersed in 900 ml of ethanol in order to obtain a 15 g/l suspension capable of carrying out an electrophoretic deposition.

Agglomerates of about 200 nm consisting of 10 nm primary Li_3PO_4 particles were thus obtained suspended in ethanol.

Porous thin layers of Li_3PO_4 were then deposited by electrophoresis on the surface of the anodes and cathodes previously prepared by applying an electric field of 20V/cm to the Li_3PO_4 nanoparticle suspension previously obtained, for 90 seconds to obtain a layer of about 2 μm . The layer was then air-dried at 120°C then a calcination treatment at 350°C for 120 minutes was performed on this previously dried layer in order to remove any trace of organic residue.

c) Assembly of the electrodes and the separator

After having deposited 2 μm of porous Li_3PO_4 on each of the electrodes ($\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) previously prepared, both subsystems were stacked in such a way that the

Li₃PO₄ films are in contact. This stack was then hot-pressed in a vacuum between two planar plates. To do this, the stack was first placed at a pressure of 5 MPa then vacuum-dried for 30 minutes at 10⁻³ bar. The plates of the press were then heated at 550°C with a rate of 0.4°C/second. At 550°C, the stack was then thermo-compressed at a pressure of 45 MPa for 20 minutes, then the system was cooled to ambient temperature. Then, the assembly was dried at 120°C for 48 hours in a vacuum (10 mbar).

d) Impregnation of the separator by a liquid electrolyte

This assembly was then impregnated, in an anhydrous atmosphere, by dipping in an electrolytic solution comprising PYR14TFSI, and 0.7 M LiTFSI. PYR14TFSI is the standard abbreviation of 1-butyl-1-methylpyrrolidinium bis(trifluoro-methanesulfonyl)imide. LITFSI is the standard abbreviation of lithium bis-trifluoromethanesulfonimide (CAS No.: 90076-65-6). This ionic liquid enters instantaneously by capillarity in the porosities of the separator. Each of the two ends of the system was kept immersed for 5 minutes in a drop of the electrolytic mixture.

It is noted that in an industrial manufacturing method, the impregnation is performed after encapsulating the battery, and followed by the production of the electrical contact members.

As a general rule, the battery according to the invention can be a lithium ion microbattery. In particular, it can be designed and dimensioned so as to have a capacitance less than or equal to about 1 mA h (commonly referred to as a "microbattery"). Typically, the microbatteries are designed so as to be compatible with microelectronic manufacturing methods.

These microbatteries can be produced:

- either solely with layers according to the invention, of "all-solid-state type, i.e. devoid of impregnated liquid or pasty phases (said liquid or pasty phases optionally being a lithium ion conducting medium, capable of acting as an electrolyte),
- or with electrodes according to the invention and mesoporous "all-solid-state" type separators, impregnated with a liquid or pasty phase, typically a lithium ion conducting medium, which spontaneously enters the inside of the layer and which no longer comes out of this layer, such that this layer can be considered as quasi-solid,

– or with electrodes according to the invention and impregnated porous separators (i.e. layers having a lattice of open pores which can be impregnated with a liquid or pasty phase, and which gives these layers wet properties).

5 Different aspects of the invention

As is clear from the description given, the present invention has several aspects, features and combinations of features which are compiled in a summarised manner hereinafter.

A first aspect of the invention is a method for manufacturing a dense layer, which comprises the steps of:

- 10 - Supplying a substrate and a suspension of non-agglomerated nanoparticles of an inorganic material P,
- Depositing a layer, on said substrate, using the suspension of primary nanoparticles of a material P;
- Drying the layer thus obtained;

- 15 - Densifying the dried layer by mechanical compression and/or heat treatment,
- knowing that the third and the fourth step can be performed at least partially at the same time, or during a temperature ramp;

 said method being characterised in that said suspension of non-agglomerated nanoparticles of material P comprises nanoparticles of material P having a size distribution, said size being characterised by the value of D_{50} thereof, such that:

20 the distribution comprises nanoparticles of material P of a first size D1 between 20 nm and 50 nm, and nanoparticles of material P of a second size D2 characterised by a value D_{50} at least five times less than that of D1.

 According to an alternative, the distribution has a mean size of nanoparticles of material P less than 50 nm, and a standard deviation to mean size ratio greater than 0.6.

25 less than 50 nm, and a standard deviation to mean size ratio greater than 0.6.

 According to a first variant of this first aspect, said suspension of non-agglomerated nanoparticles of material P comprises nanoparticles of material P of a first size D1 between 20 nm and 50 nm, and nanoparticles of material P of a second size D2 characterised by a value D_{50} at least five times less than that of D1, and said particles of size D1 represent between 50 and 75% of the total mass of nanoparticles. Preferably, the

30 size D1 represent between 50 and 75% of the total mass of nanoparticles. Preferably, the

mean diameter of the second population is at least one fifteenth of that of the first nanoparticle population, and preferably at least one twelfth.

According to a second variant of this first aspect, which is also compatible with the first variant thereof, said suspension of non-agglomerated nanoparticles of material P is obtained using a monodisperse suspension of nanoparticles of size D1.

According to a third variant of this first aspect, which is also compatible with the first and second variant thereof, the suspension of nanoparticles of size D2 is obtained using a monodisperse suspension.

According to a fourth variant of this first aspect, which is also compatible with the first, second and third variant thereof, a mixture of two nanoparticle size populations is used, such that the mean diameter of the greatest distribution does not exceed 100 nm, and preferably does not exceed 50 nm. Preferably, this first population of the largest nanoparticles has a size distribution characterised by a σ/R_{mean} ratio less than 0.6.

In a first sub-variant of this variant, preferably, said population of the largest nanoparticles represents between 50% and 75% of the dry extract of the deposition, and the second nanoparticle population represents between 50% and 25% of the dry extract of the deposition (these percentages being expressed as a mass percentage with respect to the total mass of nanoparticles in the deposition).

In a second sub-variant of this fourth variant, the mean diameter of the particles of this second population is at least 5 times smaller than that of the first nanoparticle population, and preferably the mean diameter of the second population is at least one fifteenth of that of the first nanoparticle population, and preferably at least one twelfth. Preferably, this second population has a size distribution characterised by a σ/R_{mean} ratio less than 0.6.

According to a fifth variant of this first aspect, which is also compatible with the first, second, third and fourth variant thereof, for the deposition of said dense layer, a method selected from printing techniques, particularly ink-jet and flexographic printing, electrophoresis techniques, and coating techniques, particularly roll, curtain, doctor blade, dip, or slot-die coating, is used.

According to a sixth variant of this first aspect, which is also compatible with the first, second, third, fourth and fifth variant thereof, said suspension has a viscosity, measured at 20°C, between 20 cP and 2000 cP.

According to a seventh variant of this first aspect, which is also compatible with the first, second, third, fourth, fifth and sixth variant thereof, said material P is an inorganic material, preferably selected in the group formed by:

- cathode materials, preferably selected in the group formed by:
 - 5 - the oxides LiMn_2O_4 , $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ where $0 < x < 0.15$, LiCoO_2 , LiNiO_2 , $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, $\text{LiMn}_{1.5}\text{Ni}_{0.5-x}\text{X}_x\text{O}_4$ where X is selected from Al, Fe, Cr, Co, Rh, Nd, other rare earths such as Sc, Y, Lu, La, Ce, Pr, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and where $0 < x < 0.1$, $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ where $\text{M} = \text{Er, Dy, Gd, Tb, Yb, Al, Y, Ni, Co, Ti, Sn, As, Mg}$ or a mixture of these compounds and where $0 < x < 0.4$,
 10 LiFeO_2 , $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ where $0 \leq x < 0.15$, $\text{LiNi}_{1/x}\text{Co}_{1/y}\text{Mn}_{1/z}\text{O}_2$ where $x+y+z=10$;
 - the phosphates LiFePO_4 , LiMnPO_4 , LiCoPO_4 , LiNiPO_4 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; the phosphates of formula $\text{LiMM}'\text{PO}_4$, where M and M' ($\text{M} \neq \text{M}'$) are selected from Fe, Mn, Ni, Co, V;
 - 15 - all lithiated forms of the following chalcogenides: V_2O_5 , V_3O_8 , TiS_2 , titanium oxysulphides (TiO_yS_z where $z=2-y$ and $0.3 \leq y \leq 1$), tungsten oxysulphides (WO_yS_z where $0.6 < y < 3$ and $0.1 < z < 2$), CuS , CuS_2 , preferably $\text{Li}_x\text{V}_2\text{O}_5$ where $0 < x \leq 2$, $\text{Li}_x\text{V}_3\text{O}_8$ where $0 < x \leq 1.7$, Li_xTiS_2 where $0 < x \leq 1$, titanium and lithium oxysulphides $\text{Li}_x\text{TiO}_y\text{S}_z$ where $z = 2-y$, $0.3 \leq y \leq 1$, $\text{Li}_x\text{WO}_y\text{S}_z$, Li_xCuS , Li_xCuS_2 ;
 - 20 - anode materials, preferably selected in the group formed by:
 - carbon nanotubes, graphene, graphite;
 - lithiated iron phosphate (of typical formula LiFePO_4);
 - mixed silicon and tin oxynitrides (of typical formula $\text{Si}_a\text{Sn}_b\text{O}_y\text{N}_z$ where $a>0$, $b>0$, $a+b \leq 2$, $0 < y \leq 4$, $0 < z \leq 3$) (also known as SiTON), and in particular $\text{SiSn}_{0.87}\text{O}_{1.2}\text{N}_{1.72}$;
 - 25 as well as oxynitrides-carbides of typical formula $\text{Si}_a\text{Sn}_b\text{C}_c\text{O}_y\text{N}_z$ where $a > 0$, $b > 0$, $a+b \leq 2$, $0 < c < 10$, $0 < y < 24$, $0 < z < 17$;
 - nitrides of type Si_xN_y (in particular where $x=3$ and $y=4$), Sn_xN_y (in particular where $x=3$ and $y=4$), Zn_xN_y (in particular where $x=3$ and $y=2$), $\text{Li}_{3-x}\text{M}_x\text{N}$ (where $0 \leq x \leq 0.5$ for $\text{M}=\text{Co}$, $0 \leq x \leq 0.6$ for $\text{M}=\text{Ni}$, $0 \leq x \leq 0.3$ for $\text{M}=\text{Cu}$); $\text{Si}_{3-x}\text{M}_x\text{N}_4$ where $\text{M}=\text{Co}$ or Fe and $0 \leq x \leq 3$.
 - 30 - the oxides SnO_2 , SnO , Li_2SnO_3 , SnSiO_3 , Li_xSiO_y ($x \geq 0$ and $2 > y > 0$), $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiNb_2O_7 , Co_3O_4 , $\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ and TiO_2 ,
 - composite oxides TiNb_2O_7 comprising between 0% and 10% by mass of carbon, preferably the carbon being selected from graphene and carbon nanotubes;
 - 35 - electrolyte materials, preferably selected in the group formed by:

- garnets of formula $\text{Li}_d\text{A}^1_x\text{A}^2_y(\text{TO}_4)_z$ where A^1 represents a cation of degree of oxidation +II, preferably Ca, Mg, Sr, Ba, Fe, Mn, Zn, Y, Gd; and where A^2 represents a cation of degree of oxidation +III, preferably Al, Fe, Cr, Ga, Ti, La; and where (TO_4) represents an anion wherein T is an atom of degree of oxidation +IV, located at the centre of a tetrahedron formed by oxygen atoms, and wherein TO_4 represents advantageously the silicate or zirconate anion, knowing that all or part of the elements T of a degree of oxidation +IV can be replaced by atoms of a degree of oxidation +III or +V, such as Al, Fe, As, V, Nb, In, Ta; knowing that: d is between 2 and 10, preferably between 3 and 9, and even more preferably between 4 and 8; x is between 2.6 and 3.4 (preferably between 2.8 and 3.2); y is between 1.7 and 2.3 (preferably between 1.9 and 2.1) and z is between 2.9 and 3.1;
- garnets, preferably selected from: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$; $\text{Li}_6\text{La}_2\text{BaTa}_2\text{O}_{12}$; $\text{Li}_{5.5}\text{La}_3\text{Nb}_{1.75}\text{In}_{0.25}\text{O}_{12}$; $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ where M = Nb or Ta or a mixture of these two compounds; $\text{Li}_{7-x}\text{Ba}_x\text{La}_{3-x}\text{M}_2\text{O}_{12}$ where $0 \leq x \leq 1$ and M = Nb or Ta or a mixture of the two compounds; $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{M}_x\text{O}_{12}$ where $0 \leq x \leq 2$ and M = Al, Ga or Ta or a mixture of two or three of these compounds;
- lithiated phosphates, preferably selected from: lithiated phosphates of the type NaSICON, Li_3PO_4 ; LiPO_3 ; $\text{Li}_3\text{Al}_{0.4}\text{Sc}_{1.6}(\text{PO}_4)_3$ referred to as "LASP"; $\text{Li}_{1.2}\text{Zr}_{1.9}\text{Ca}_{0.1}(\text{PO}_4)_3$; $\text{LiZr}_2(\text{PO}_4)_3$; $\text{Li}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$ where $1.8 < x < 2.3$; $\text{Li}_{1+6x}\text{Zr}_2(\text{P}_{1-x}\text{B}_x\text{O}_4)_3$ where $0 \leq x \leq 0.25$; $\text{Li}_3(\text{Sc}_{2-x}\text{M}_x)(\text{PO}_4)_3$ where M=Al or Y and $0 \leq x \leq 1$; $\text{Li}_{1+x}\text{M}_x(\text{Sc})_{2-x}(\text{PO}_4)_3$ where M = Al, Y, Ga or a mixture of the three compounds and $0 \leq x \leq 0.8$; $\text{Li}_{1+x}\text{M}_x(\text{Ga}_{1-y}\text{Sc}_y)_{2-x}(\text{PO}_4)_3$ where $0 \leq x \leq 0.8$; $0 \leq y \leq 1$ and M= Al or Y or a mixture of both compounds; $\text{Li}_{1+x}\text{M}_x(\text{Ga})_{2-x}(\text{PO}_4)_3$ where M = Al, Y or a mixture of both compounds and $0 \leq x \leq 0.8$; $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ where $0 \leq x \leq 1$ referred to as "LATP"; or $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ where $0 \leq x \leq 1$ referred to as "LAGP"; or $\text{Li}_{1+x+z}\text{M}_x(\text{Ge}_{1-y}\text{Ti}_y)_{2-x}\text{Si}_z\text{P}_{3-z}\text{O}_{12}$ where $0 \leq x \leq 0.8$ and $0 \leq y \leq 1.0$ and $0 \leq z \leq 0.6$ and M= Al, Ga or Y or a mixture of two or three of these compounds; $\text{Li}_{3+y}(\text{Sc}_{2-x}\text{M}_x)\text{Q}_y\text{P}_{3-y}\text{O}_{12}$ where M = Al and/or Y and Q = Si and/or Se, $0 \leq x \leq 0.8$ and $0 \leq y \leq 1$; or $\text{Li}_{1+x+y}\text{M}_x\text{Sc}_{2-x}\text{Q}_y\text{P}_{3-y}\text{O}_{12}$ where M = Al, Y, Ga or a mixture of the three compounds and Q = Si and/or Se, $0 \leq x \leq 0.8$ and $0 \leq y \leq 1$; or $\text{Li}_{1+x+y+z}\text{M}_x(\text{Ga}_{1-y}\text{Sc}_y)_{2-x}\text{Q}_z\text{P}_{3-z}\text{O}_{12}$ where $0 \leq x \leq 0.8$, $0 \leq y \leq 1$, $0 \leq z \leq 0.6$ where M = Al or Y or a mixture of both compounds and Q= Si and/or Se; or $\text{Li}_{1+x}\text{Zr}_{2-x}\text{B}_x(\text{PO}_4)_3$ where $0 \leq x \leq 0.25$; or $\text{Li}_{1+x}\text{Zr}_{2-x}\text{Ca}_x(\text{PO}_4)_3$ where $0 \leq x \leq 0.25$; or $\text{Li}_{1+x}\text{M}^3_x\text{M}_{2-x}\text{P}_3\text{O}_{12}$ where $0 \leq x \leq 1$ and $\text{M}^3 = \text{Cr, V, Ca, B, Mg, Bi and/or Mo}$, M = Sc, Sn, Zr, Hf, Se or Si, or a mixture of these compounds; $\text{Li}_{1+2x}\text{Ca}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ where $0 \leq x \leq 0.25$;

- lithiated borates, preferably selected from: $\text{Li}_3(\text{Sc}_{2-x}\text{M}_x)(\text{BO}_3)_3$ where $\text{M}=\text{Al}$ or Y and $0 \leq x \leq 1$; $\text{Li}_{1+x}\text{M}_x(\text{Sc})_{2-x}(\text{BO}_3)_3$ where $\text{M} = \text{Al}, \text{Y}, \text{Ga}$ or a mixture of the three compounds and $0 \leq x \leq 0.8$; $\text{Li}_{1+x}\text{M}_x(\text{Ga}_{1-y}\text{Sc}_y)_{2-x}(\text{BO}_3)_3$ where $0 \leq x \leq 0.8$, $0 \leq y \leq 1$ and $\text{M} = \text{Al}$ or Y ; $\text{Li}_{1+x}\text{M}_x(\text{Ga})_{2-x}(\text{BO}_3)_3$ where $\text{M} = \text{Al}, \text{Y}$ or a mixture of both compounds and $0 \leq x \leq 0.8$; Li_3BO_3 , $\text{Li}_3\text{BO}_3\text{-Li}_2\text{SO}_4$, $\text{Li}_3\text{BO}_3\text{-Li}_2\text{SiO}_4$, $\text{Li}_3\text{BO}_3\text{-Li}_2\text{SiO}_4\text{-Li}_2\text{SO}_4$;
- oxynitrides, preferably selected from $\text{Li}_3\text{PO}_{4-x}\text{N}_{2x/3}$, $\text{Li}_4\text{SiO}_{4-x}\text{N}_{2x/3}$, $\text{Li}_4\text{GeO}_{4-x}\text{N}_{2x/3}$ where $0 < x < 4$ or $\text{Li}_3\text{BO}_{3-x}\text{N}_{2x/3}$ where $0 < x < 3$;
- lithiated compounds based on lithium and phosphorus oxynitride, referred to as "LiPON", in the form of $\text{Li}_x\text{PO}_y\text{N}_z$ where $x \sim 2.8$ and $2y+3z \sim 7.8$ and $0.16 \leq z \leq 0.4$, and in particular $\text{Li}_{2.9}\text{PO}_{3.3}\text{N}_{0.46}$, but also the compounds $\text{Li}_w\text{PO}_x\text{N}_y\text{S}_z$ where $2x+3y+2z = 5 = w$ or the compounds $\text{Li}_w\text{PO}_x\text{N}_y\text{S}_z$ where $3.2 \leq x \leq 3.8$, $0.13 \leq y \leq 0.4$, $0 \leq z \leq 0.2$, $2.9 \leq w \leq 3.3$ or the compounds in the form of $\text{Li}_t\text{P}_x\text{Al}_y\text{O}_u\text{N}_v\text{S}_w$ where $5x+3y=5$, $2u+3v+2w=5+t$, $2.9 \leq t \leq 3.3$, $0.84 \leq x \leq 0.94$, $0.094 \leq y \leq 0.26$, $3.2 \leq u \leq 3.8$, $0.13 \leq v \leq 0.46$, $0 \leq w \leq 0.2$;
- materials based on lithium phosphorus or boron oxynitrides, referred to respectively as "LiPON" and "LiBON", optionally also containing silicon, sulphur, zirconium, aluminium, or a combination of aluminium, boron, sulphur and/or silicon, and boron for materials based on lithium phosphorus oxynitrides;
- lithiated compounds based on lithium, phosphorus and silicon oxynitride referred to as "LiSiPON", and in particular $\text{Li}_{1.9}\text{Si}_{0.28}\text{P}_{1.0}\text{O}_{1.1}\text{N}_{1.0}$;
- lithium oxynitrides of the types LiBON, LiBSO, LiSiPON, LiSON, thio-LiSiCON, LiPONB (where B, P and S represent respectively boron, phosphorus and sulphur);
- lithium oxynitrides of the type LiBSO such as $(1-x)\text{LiBO}_2\text{-xLi}_2\text{SO}_4$ where $0.4 \leq x \leq 0.8$;
- lithiated oxides, preferably selected from $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ or $\text{Li}_{5+x}\text{La}_3(\text{Zr}_x\text{A}_{2-x})\text{O}_{12}$ where $\text{A} = \text{Sc}, \text{Y}, \text{Al}, \text{Ga}$ and $1.4 \leq x \leq 2$ or $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ or $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ where $0 \leq x \leq 0.16$ (LLTO);
- silicates, preferably selected from $\text{Li}_2\text{Si}_2\text{O}_5$, Li_2SiO_3 , $\text{Li}_2\text{Si}_2\text{O}_6$, LiAlSiO_4 , Li_4SiO_4 , $\text{LiAlSi}_2\text{O}_6$;
- anti-perovskite type solid electrolytes selected from: Li_3OA where A is a halide or halide mixture, preferably at least one of the elements selected from $\text{F}, \text{Cl}, \text{Br}, \text{I}$ or a mixture of two or three or four of these elements; $\text{Li}_{(3-x)}\text{M}_{x/2}\text{OA}$ where $0 < x \leq 3$, M is a divalent metal, preferably at least one of the elements selected from $\text{Mg}, \text{Ca}, \text{Ba}, \text{Sr}$ or a mixture of two or three or four of these elements, A is a halide or halide

mixture, preferably at least one of the elements selected from F, Cl, Br, I or a mixture of two or three or four of these elements; $\text{Li}_{(3-x)}\text{M}^3_{x/3}\text{OA}$ where $0 \leq x \leq 3$, M^3 is a trivalent metal, A is a halide or a halide mixture, preferably at least one of the elements selected from F, Cl, Br, I or a mixture of two or three or four of these elements; or $\text{LiCOX}_z\text{Y}_{(1-z)}$, where X and Y are halides as mentioned above in relation to A, and $0 \leq z \leq 1$,

- the compounds $\text{La}_{0,51}\text{Li}_{0,34}\text{Ti}_{2,94}$, $\text{Li}_{3,4}\text{V}_{0,4}\text{Ge}_{0,6}\text{O}_4$, $\text{Li}_2\text{O-Nb}_2\text{O}_5$, LiAlGaSPO_4 ;
- formulations based on Li_2CO_3 , B_2O_3 , Li_2O , $\text{Al}(\text{PO}_3)_3\text{LiF}$, P_2S_3 , Li_2S , Li_3N , $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$, $\text{Li}_{3,6}\text{Ge}_{0,6}\text{V}_{0,4}\text{O}_4$, $\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_{3,25}\text{Ge}_{0,25}\text{P}_{0,25}\text{S}_4$, $\text{Li}_{1,3}\text{Al}_{0,3}\text{Ti}_{1,7}(\text{PO}_4)_3$, $\text{Li}_{1+x}\text{Al}_x\text{M}_{2-x}(\text{PO}_4)_3$ (where M = Ge, Ti, and/or Hf, and where $0 < x < 1$), $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (where $0 \leq x \leq 1$ and $0 \leq y \leq 1$).

According to an eighth variant of this first aspect, which is also compatible with the first, second, third, fourth, fifth, sixth and seventh variant thereof, said nanoparticles of an inorganic material P comprise nanoparticles composed of a core and a shell, the core being formed of said inorganic material P, whereas the shell is formed of another material, which is preferably organic, and even more preferably polymeric.

In a first sub-variant of this eighth variant, said shell is formed of a material which is an electronic conductor.

In a second sub-variant of this eighth variant, said shell is formed of a material which is an electronic insulator and a cation conductor, in particular a lithium ion conductor.

In a third sub-variant of this eighth variant, said shell is formed of a material which is an electronic conductor and a cation conductor, in particular a lithium ion conductor.

According to a ninth variant of this first aspect, which is also compatible with the first, second, third, fourth, fifth, sixth, seventh and eighth variant, said nanoparticles of an inorganic material P (or, in the case of the eighth variant, said core made of inorganic material P of said nanoparticles) were prepared in suspension by precipitation.

A second aspect of the invention is a method for manufacturing at least one dense layer in a lithium ion battery, said method for manufacturing said dense layer being that according to the first aspect of the invention, with all the variants and all the sub-variants described in relation to this first aspect of the invention.

According to a first variant of this second aspect, said material P is selected such that said dense layer can function as an anode in a lithium ion battery.

According to a second variant of this second aspect, said material P is selected such that said dense layer can function as a cathode in a lithium ion battery.

- 5 According to a third variant of this second aspect, which is also compatible with the first and the second variant thereof, said material P is selected such that said dense layer can function as an electrolyte in a lithium ion battery.

- 10 A third aspect of the invention is a method for manufacturing at least one dense layer in a lithium ion battery, said dense layer being capable of being obtained with the method according to the first aspect of the invention, with all the variants and all the sub-variants described in relation to this first aspect of the invention.

According to a first variant of this third aspect, said material P is selected such that said dense layer can function as an anode in a lithium ion battery.

- 15 According to a second variant of this third aspect, which is also compatible with the first variant thereof, said material P is selected such that said dense layer can function as a cathode in a lithium ion battery.

- 20 According to a third variant of this third aspect, which is also compatible with the first and the second variant thereof, said material P is selected such that said dense layer can function as an electrolyte in a lithium ion battery.

- 25 A fourth aspect of the invention is a method for manufacturing a lithium ion battery, said battery comprising at least one dense electrode layer deposited with the method according to the first aspect of the invention, with all the variants and all the sub-variants described in relation to this first aspect of the invention, and wherein a porous layer intended to form the separator is also deposited, preferably using an electrolyte material according to the seventh variant of the first aspect of the invention.

- 30 According to a first variant of this fourth aspect, said porous layer is a mesoporous layer, preferably with a mesoporous volume between 25% and 75%, and even more preferably between 30% and 60%.

According to a second variant of this fourth aspect, which is also compatible with the first variant thereof, the method for depositing said porous layer is a method selected preferably in the group formed by: electrophoresis, a printing method, selected preferably

from ink-jet printing and flexographic printing, and a coating method selected preferably from roll coating, curtain coating, doctor blade coating, slot-die coating, dip-coating, knowing that in any case, the deposition is carried out using a suspension of nanoparticle aggregates or agglomerates.

- 5 According to a third variant of this fourth aspect, which is also compatible with the first and second variant thereof, a concentrated suspension containing nanoparticle agglomerates is used for depositing said porous layer.

10 According to a fourth variant of this fourth aspect, which is also compatible with the first, second and third variant thereof, a colloidal suspension is used for depositing said porous layer comprising aggregates or agglomerates of nanoparticles of at least one inorganic material, of mean primary diameter D_{50} between 2 nm and 100 nm, preferably between 2 nm and 60 nm, said aggregates or agglomerates typically having a mean diameter D_{50} between 50 nm and 300 nm, and preferably between 100 nm and 200 nm.

- 15 According to a fifth variant of this fourth aspect, which is also compatible with the first, second, third and fourth variant thereof, said layer thus obtained is dried and it is consolidated, by pressing and/or heating, to obtain a porous layer, preferably mesoporous and inorganic.

20 According to a sixth variant of this fourth aspect, which is also compatible with the first, second, third, fourth and fifth variant thereof, said porous layer is deposited on said dense layer.

According to a seventh variant of this fourth aspect, which is also compatible with the first, second, third, fourth, fifth and sixth variant thereof, said dense layer is deposited on said mesoporous layer.

- 25 According to an eighth variant of this fourth aspect, which is also compatible with the first, second, third, fourth, fifth, sixth and seventh variant thereof, a second electrode layer is deposited on said porous layer.

According to a first sub-variant of this eighth variant, said second electrode layer is a dense electrode, deposited with a method according to the first aspect of the invention.

- 30 According to a second sub-variant of this eighth variant, said second electrode layer is a porous electrode, preferably prepared according to the method for preparing a porous separating layer in relation to this fourth aspect of the invention, and particularly according to the first, second, third, fourth, and fifth variant thereof, the separator material being

replaced by a suitable electrode material, and preferably using an anode material or a cathode material according to the seventh variant of the first aspect of the invention.

According to a ninth variant of this fourth aspect, which is also compatible with the first, second, third, fourth, fifth, sixth, seventh and eighth variant thereof, said porous
 5 separating layer is impregnated with mobile lithium ion carrier liquid, which is preferably selected in the group formed by:

- o an electrolyte composed of at least one aprotic solvent and at least one lithium salt;
- o an electrolyte composed of at least one ionic liquid or ionic polyliquid and at least one lithium salt;
- 10 o a mixture of at least one aprotic solvent and at least one ionic liquid or ionic polyliquid and at least one lithium salt;
- o a polymer rendered an ionic conductor by adding at least one lithium salt; and
- o a polymer rendered an ionic conductor by adding a liquid electrolyte, either in the polymer phase, or in the mesoporous structure,
- 15 said polymer being preferably selected in the group formed by poly(ethylene oxide), poly(propylene oxide), polydimethylsiloxane, polyacrylonitrile, poly(methyl methacrylate), poly(vinyl chloride), poly(vinylidene fluoride), PVDF-hexafluoropropylene.

A fifth aspect of the invention is a dense layer capable of being obtained with the method according to the first aspect of the invention, with all the variants and all the sub-variants
 20 described in relation to this first aspect of the invention.

According to a first variant of this fifth aspect, said material P is selected such that said dense layer can function as an anode in a lithium ion battery.

According to a second variant of this fifth aspect, which is also compatible with the first variant thereof, said material P is selected such that said dense layer can function as a
 25 cathode in a lithium ion battery.

According to a third variant of this fifth aspect, which is also compatible with the first and the second variant thereof, said material P is selected such that said dense layer can function as an electrolyte in a lithium ion battery.

According to a fourth variant of this fifth aspect, which is also compatible with the first,
 30 second and third variant thereof, said dense layer has a density of at least 90% of the theoretical density, preferably at least 95% of the theoretical density, and even more preferably at least 96% of the theoretical density, and optimally at least 97% of the theoretical density.

A sixth aspect of the invention is a dense layer in a lithium ion battery capable of being obtained with the method according to the first aspect of the invention, with all the variants and all the sub-variants described in relation to this first aspect of the invention.

- 5 According to a first variant of this sixth aspect, said material P is selected such that said dense layer can function as an anode in a lithium ion battery.

According to a second variant of this sixth aspect, which is also compatible with the first variant thereof, said material P is selected such that said dense layer can function as a cathode in a lithium ion battery.

- 10 According to a third variant of this sixth aspect, which is also compatible with the first and the second variant thereof, said material P is selected such that said dense layer can function as an electrolyte in a lithium ion battery.

- A seventh aspect of the invention is a lithium ion battery with a capacitance not exceeding
15 1 mA h, referred to here as a "microbattery", comprising at least one dense layer according to the fifth aspect of the invention, with all the variants and all the sub-variants described in relation to this fifth aspect of the invention.

According to a first variant of this seventh aspect, said microbattery comprises an anode which is a dense layer according to the fifth aspect of the invention.

- 20 According to a second variant of this seventh aspect, said microbattery comprises a cathode which is a dense layer according to the fifth aspect of the invention.

According to a third variant of this seventh aspect, said microbattery comprises an anode and a cathode which are dense layers according to the fifth aspect of the invention.

- 25 According to a fourth variant of this seventh aspect, said microbattery comprises an anode and a cathode and an electrolyte which are dense layers according to the fifth aspect of the invention.

According to a fourth variant of this seventh aspect, which is also compatible with the first, second and third variant thereof, said microbattery comprises a separator which is a porous layer according to the fourth aspect of the invention.

CLAIMS

1. Method for manufacturing a dense layer, comprising the steps of:
 - (i) Supplying a substrate and a suspension of non-agglomerated nanoparticles of a material P;
 - 5 (ii) Depositing a layer, on said substrate, using the suspension of primary nanoparticles of a material P;
 - (iii) Drying the layer thus obtained;
 - (iv) Densifying the dried layer by mechanical compression and/or heat treatment,

knowing that steps (iii) and (iv) can be performed at least partially at the same time, or

10 during a temperature ramp;

said method being characterised in that the suspension of non-agglomerated nanoparticles of material P comprises nanoparticles of material P having a size distribution, said size being characterised by the value of D_{50} thereof, such that:

 - the distribution comprises nanoparticles of material P of a first size D1 between 20
 - 15 nm and 50 nm, and nanoparticles of material P of a second size D2 characterised by a value D_{50} at least five times less than that of D1; or
 - the distribution has a mean size of nanoparticles of material P less than 50 nm, and a standard deviation to mean size ratio greater than 0.6.
2. Method according to claim 1, wherein said suspension of non-agglomerated
- 20 nanoparticles of material P comprises nanoparticles of material P of a first size D1 between 20 nm and 50 nm, and nanoparticles of material P of a second size D2 characterised by a value D_{50} at least five times less than that of D1, and said particles of size D1 represent between 50 and 75% of the total mass of nanoparticles.
3. Method according to claim 2, wherein the mean diameter of nanoparticles of the
- 25 second size is at least one fifteenth of that of nanoparticle of the first size, and preferably at least one twelfth.
4. Method according to any of claims 1 to 3, characterised in that said suspension of non-agglomerated nanoparticles of material P is obtained using a monodisperse suspension of size D1.
- 30 5. Method according to one of claims 1 to 4, characterised in that the suspension of nanoparticles of size D2 is obtained using a monodisperse suspension.

6. Method according to any one of claims 1 to 5, characterised in that the deposition of the dense thin layer is performed electrophoretically, by the dip-coating method, by the ink-jet printing method, by roll coating, by curtain coating or by doctor blade coating.
- 5 7. Method according to any one of claims 1 to 6, characterised in that said suspension has a viscosity, measured at 20°C, between 20 cP and 2000 cP.
8. Method according to any one of claims 1 to 7, characterised in that said material P is an inorganic material, preferably selected in the group formed by:
 - the oxides LiMn_2O_4 , $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ where $0 < x < 0.15$, LiCoO_2 , LiNiO_2 ,
 10 $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, $\text{LiMn}_{1.5}\text{Ni}_{0.5-x}\text{X}_x\text{O}_4$ where X is selected from Al, Fe, Cr, Co, Rh, Nd, other rare earths such as Sc, Y, Lu, La, Ce, Pr, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and where $0 < x < 0.1$, $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ where M = Er, Dy, Gd, Tb, Yb, Al, Y, Ni, Co, Ti, Sn, As, Mg or a mixture of these compounds and where $0 < x < 0.4$, LiFeO_2 , $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ where $0 \leq x < 0.15$,
 15 $\text{LiNi}_{1/x}\text{Co}_{1/y}\text{Mn}_{1/z}\text{O}_2$ where $x+y+z=10$;
 - the phosphates LiFePO_4 , LiMnPO_4 , LiCoPO_4 , LiNiPO_4 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; the phosphates of formula $\text{LiMM}'\text{PO}_4$, where M and M' ($M \neq M'$) are selected from Fe, Mn, Ni, Co, V;
 - all lithiated forms of the following chalcogenides: V_2O_5 , V_3O_8 , TiS_2 , titanium
 20 oxysulphides (TiO_yS_z where $z=2-y$ and $0.3 \leq y \leq 1$), tungsten oxysulphides (WO_yS_z where $0.6 < y < 3$ and $0.1 < z < 2$), CuS , CuS_2 , preferably $\text{Li}_x\text{V}_2\text{O}_5$ where $0 < x \leq 2$, $\text{Li}_x\text{V}_3\text{O}_8$ where $0 < x \leq 1.7$, Li_xTiS_2 where $0 < x \leq 1$, titanium and lithium oxysulphides $\text{Li}_x\text{TiO}_y\text{S}_z$ where $z = 2-y$, $0.3 \leq y \leq 1$, $\text{Li}_x\text{WO}_y\text{S}_z$, Li_xCuS , Li_xCuS_2 ;
 - carbon nanotubes, graphene, graphite;
 - 25 - lithiated iron phosphate (of typical formula LiFePO_4);
 - mixed silicon and tin oxynitrides (of typical formula $\text{Si}_a\text{Sn}_b\text{O}_y\text{N}_z$ where $a>0$, $b>0$, $a+b \leq 2$, $0 < y \leq 4$, $0 < z \leq 3$) (also known as SiTON), and in particular $\text{SiSn}_{0.87}\text{O}_{1.2}\text{N}_{1.72}$; as well as oxynitrides-carbides of typical formula $\text{Si}_a\text{Sn}_b\text{C}_c\text{O}_y\text{N}_z$ where $a > 0$, $b > 0$, $a+b \leq 2$, $0 < c < 10$, $0 < y < 24$, $0 < z < 17$;
 - 30 - nitrides of type Si_xN_y (in particular where $x=3$ and $y=4$), Sn_xN_y (in particular where $x=3$ and $y=4$), Zn_xN_y (in particular where $x=3$ and $y=2$), $\text{Li}_{3-x}\text{M}_x\text{N}$ (where $0 \leq x \leq 0.5$ for $M=\text{Co}$, $0 \leq x \leq 0.6$ for $M=\text{Ni}$, $0 \leq x \leq 0.3$ for $M=\text{Cu}$); $\text{Si}_{3-x}\text{M}_x\text{N}_4$ where $M=\text{Co}$ or Fe and $0 \leq x \leq 3$.
 - the oxides SnO_2 , SnO , Li_2SnO_3 , SnSiO_3 , Li_xSiO_y ($x \geq 0$ and $2 > y > 0$), $\text{Li}_4\text{Ti}_5\text{O}_{12}$,
 35 TiNb_2O_7 , Co_3O_4 , $\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ and TiO_2 ,

- composite oxides TiNb_2O_7 comprising between 0% and 10% by mass of carbon, preferably the carbon being selected from graphene and carbon nanotubes;
- garnets of formula $\text{Li}_d\text{A}^1_x\text{A}^2_y(\text{TO}_4)_z$ where A^1 represents a cation of degree of oxidation +II, preferably Ca, Mg, Sr, Ba, Fe, Mn, Zn, Y, Gd; and where A^2 represents a cation of degree of oxidation +III, preferably Al, Fe, Cr, Ga, Ti, La; and where (TO_4) represents an anion wherein T is an atom of degree of oxidation +IV, located at the centre of a tetrahedron formed by oxygen atoms, and wherein TO_4 represents advantageously the silicate or zirconate anion, knowing that all or part of the elements T of a degree of oxidation +IV can be replaced by atoms of a degree of oxidation +III or +V, such as Al, Fe, As, V, Nb, In, Ta; knowing that: d is between 2 and 10, preferably between 3 and 9, and even more preferably between 4 and 8; x is between 2.6 and 3.4 (preferably between 2.8 and 3.2); y is between 1.7 and 2.3 (preferably between 1.9 and 2.1) and z is between 2.9 and 3.1;
- garnets, preferably selected from: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$; $\text{Li}_6\text{La}_2\text{BaTa}_2\text{O}_{12}$; $\text{Li}_{5.5}\text{La}_3\text{Nb}_{1.75}\text{In}_{0.25}\text{O}_{12}$; $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ where M = Nb or Ta or a mixture of these two compounds; $\text{Li}_{7-x}\text{Ba}_x\text{La}_{3-x}\text{M}_2\text{O}_{12}$ where $0 \leq x \leq 1$ and M = Nb or Ta or a mixture of the two compounds; $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{M}_x\text{O}_{12}$ where $0 \leq x \leq 2$ and M = Al, Ga or Ta or a mixture of two or three of these compounds;
- lithiated phosphates, preferably selected from: lithiated phosphates of the type NaSICON, Li_3PO_4 ; LiPO_3 ; $\text{Li}_3\text{Al}_{0.4}\text{Sc}_{1.6}(\text{PO}_4)_3$ referred to as "LASP"; $\text{Li}_{1.2}\text{Zr}_{1.9}\text{Ca}_{0.1}(\text{PO}_4)_3$; $\text{LiZr}_2(\text{PO}_4)_3$; $\text{Li}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$ where $1.8 < x < 2.3$; $\text{Li}_{1+6x}\text{Zr}_2(\text{P}_{1-x}\text{B}_x\text{O}_4)_3$ where $0 \leq x \leq 0.25$; $\text{Li}_3(\text{Sc}_{2-x}\text{M}_x)(\text{PO}_4)_3$ where M=Al or Y and $0 \leq x \leq 1$; $\text{Li}_{1+x}\text{M}_x(\text{Sc})_{2-x}(\text{PO}_4)_3$ where M = Al, Y, Ga or a mixture of the three compounds and $0 \leq x \leq 0.8$; $\text{Li}_{1+x}\text{M}_x(\text{Ga}_{1-y}\text{Sc}_y)_{2-x}(\text{PO}_4)_3$ where $0 \leq x \leq 0.8$; $0 \leq y \leq 1$ and M= Al or Y or a mixture of both compounds; $\text{Li}_{1+x}\text{M}_x(\text{Ga})_{2-x}(\text{PO}_4)_3$ where M = Al, Y or a mixture of both compounds and $0 \leq x \leq 0.8$; $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ where $0 \leq x \leq 1$ referred to as "LATP"; or $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ where $0 \leq x \leq 1$ referred to as "LAGP"; or $\text{Li}_{1+x+z}\text{M}_x(\text{Ge}_{1-y}\text{Ti}_y)_{2-x}\text{Si}_z\text{P}_{3-z}\text{O}_{12}$ where $0 \leq x \leq 0.8$ and $0 \leq y \leq 1.0$ and $0 \leq z \leq 0.6$ and M= Al, Ga or Y or a mixture of two or three of these compounds;
- $\text{Li}_{3+y}(\text{Sc}_{2-x}\text{M}_x)\text{Q}_y\text{P}_{3-y}\text{O}_{12}$ where M = Al and/or Y and Q = Si and/or Se, $0 \leq x \leq 0.8$ and $0 \leq y \leq 1$; or $\text{Li}_{1+x+y}\text{M}_x\text{Sc}_{2-x}\text{Q}_y\text{P}_{3-y}\text{O}_{12}$ where M = Al, Y, Ga or a mixture of the three compounds and Q = Si and/or Se, $0 \leq x \leq 0.8$ and $0 \leq y \leq 1$; or $\text{Li}_{1+x+y+z}\text{M}_x(\text{Ga}_{1-y}\text{Sc}_y)_{2-x}\text{Q}_z\text{P}_{3-z}\text{O}_{12}$ where $0 \leq x \leq 0.8$, $0 \leq y \leq 1$, $0 \leq z \leq 0.6$ where M = Al or Y or a mixture of both compounds and Q= Si and/or Se; or $\text{Li}_{1+x}\text{Zr}_{2-x}\text{B}_x(\text{PO}_4)_3$ where $0 \leq x \leq 0.25$; or $\text{Li}_{1+x}\text{Zr}_{2-x}\text{Ca}_x(\text{PO}_4)_3$ where $0 \leq x \leq 0.25$; or $\text{Li}_{1+x}\text{M}^3_x\text{M}_{2-x}\text{P}_3\text{O}_{12}$

where $0 \leq x \leq 1$ and $M^3 = \text{Cr, V, Ca, B, Mg, Bi and/or Mo}$, $M = \text{Sc, Sn, Zr, Hf, Se or Si}$, or a mixture of these compounds; $\text{Li}_{1+2x}\text{Ca}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ where $0 \leq x \leq 0.25$;

- lithiated borates, preferably selected from: $\text{Li}_3(\text{Sc}_{2-x}\text{M}_x)(\text{BO}_3)_3$ where $M = \text{Al or Y}$ and $0 \leq x \leq 1$; $\text{Li}_{1+x}\text{M}_x(\text{Sc})_{2-x}(\text{BO}_3)_3$ where $M = \text{Al, Y, Ga}$ or a mixture of the three compounds and $0 \leq x \leq 0.8$; $\text{Li}_{1+x}\text{M}_x(\text{Ga}_{1-y}\text{Sc}_y)_{2-x}(\text{BO}_3)_3$ where $0 \leq x \leq 0.8$, $0 \leq y \leq 1$ and $M = \text{Al or Y}$; $\text{Li}_{1+x}\text{M}_x(\text{Ga})_{2-x}(\text{BO}_3)_3$ where $M = \text{Al, Y}$ or a mixture of both compounds and $0 \leq x \leq 0.8$; Li_3BO_3 , $\text{Li}_3\text{BO}_3\text{-Li}_2\text{SO}_4$, $\text{Li}_3\text{BO}_3\text{-Li}_2\text{SiO}_4$, $\text{Li}_3\text{BO}_3\text{-Li}_2\text{SiO}_4\text{-Li}_2\text{SO}_4$;
- oxynitrides, preferably selected from $\text{Li}_3\text{PO}_{4-x}\text{N}_{2x/3}$, $\text{Li}_4\text{SiO}_{4-x}\text{N}_{2x/3}$, $\text{Li}_4\text{GeO}_{4-x}\text{N}_{2x/3}$ where $0 < x < 4$ or $\text{Li}_3\text{BO}_{3-x}\text{N}_{2x/3}$ where $0 < x < 3$;
- lithiated compounds based on lithium and phosphorus oxynitride, referred to as "LiPON", in the form of $\text{Li}_x\text{PO}_y\text{N}_z$ where $x \sim 2.8$ and $2y+3z \sim 7.8$ and $0.16 \leq z \leq 0.4$, and in particular $\text{Li}_{2.9}\text{PO}_{3.3}\text{N}_{0.46}$, but also the compounds $\text{Li}_w\text{PO}_x\text{N}_y\text{S}_z$ where $2x+3y+2z = 5 = w$ or the compounds $\text{Li}_w\text{PO}_x\text{N}_y\text{S}_z$ where $3.2 \leq x \leq 3.8$, $0.13 \leq y \leq 0.4$, $0 \leq z \leq 0.2$, $2.9 \leq w \leq 3.3$ or the compounds in the form of $\text{Li}_t\text{P}_x\text{Al}_y\text{O}_u\text{N}_v\text{S}_w$ where $5x+3y=5$, $2u+3v+2w=5+t$, $2.9 \leq t \leq 3.3$, $0.84 \leq x \leq 0.94$, $0.094 \leq y \leq 0.26$, $3.2 \leq u \leq 3.8$, $0.13 \leq v \leq 0.46$, $0 \leq w \leq 0.2$;
- materials based on lithium phosphorus or boron oxynitrides, referred to respectively as "LiPON" and "LiBON", optionally also containing silicon, sulphur, zirconium, aluminium, or a combination of aluminium, boron, sulphur and/or silicon, and boron for materials based on lithium phosphorus oxynitrides;
- lithiated compounds based on lithium, phosphorus and silicon oxynitride referred to as "LiSiPON", and in particular $\text{Li}_{1.9}\text{Si}_{0.28}\text{P}_{1.0}\text{O}_{1.1}\text{N}_{1.0}$;
- lithium oxynitrides of the types LiBON, LiBSO, LiSiPON, LiSON, thio-LiSiCON, LiPONB (where B, P and S represent respectively boron, phosphorus and sulphur);
- lithium oxynitrides of the type LiBSO such as $(1-x)\text{LiBO}_2\text{-xLi}_2\text{SO}_4$ where $0.4 \leq x \leq 0.8$;
- lithiated oxides, preferably selected from $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ or $\text{Li}_{5+x}\text{La}_3(\text{Zr}_x\text{A}_{2-x})\text{O}_{12}$ where $A = \text{Sc, Y, Al, Ga}$ and $1.4 \leq x \leq 2$ or $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ or $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ where $0 \leq x \leq 0.16$ (LLTO);
- silicates, preferably selected from $\text{Li}_2\text{Si}_2\text{O}_5$, Li_2SiO_3 , $\text{Li}_2\text{Si}_2\text{O}_6$, LiAlSiO_4 , Li_4SiO_4 , $\text{LiAlSi}_2\text{O}_6$;
- anti-perovskite type solid electrolytes selected from: Li_3OA where A is a halide or halide mixture, preferably at least one of the elements selected from F, Cl, Br, I or a mixture of two or three or four of these elements; $\text{Li}_{(3-x)}\text{M}_{x/2}\text{OA}$ where $0 < x \leq 3$, M

- a is divalent metal, preferably at least one of the elements selected from Mg, Ca, Ba, Sr or a mixture of two or three or four of these elements, A is a halide or halide mixture, preferably at least one of the elements selected from F, Cl, Br, I or a mixture of two or three or four of these elements; $\text{Li}_{(3-x)}\text{M}^3_{x/3}\text{OA}$ where $0 \leq x \leq 3$, M^3 is a trivalent metal, A is a halide or a halide mixture, preferably at least one of the elements selected from F, Cl, Br, I or a mixture of two or three or four of these elements; or $\text{LiCOX}_z\text{Y}_{(1-z)}$, where X and Y are halides as mentioned above in relation to A, and $0 \leq z \leq 1$,
- the compounds $\text{La}_{0.51}\text{Li}_{0.34}\text{Ti}_{2.94}$, $\text{Li}_{3.4}\text{V}_{0.4}\text{Ge}_{0.6}\text{O}_4$, $\text{Li}_2\text{O-Nb}_2\text{O}_5$, LiAlGaSPO_4 ;
 - formulations based on Li_2CO_3 , B_2O_3 , Li_2O , $\text{Al}(\text{PO}_3)_3\text{LiF}$, P_2S_3 , Li_2S , Li_3N , $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$, $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$, $\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.25}\text{S}_4$, $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$, $\text{Li}_{1+x}\text{Al}_x\text{M}_{2-x}(\text{PO}_4)_3$ (where M = Ge, Ti, and/or Hf, and where $0 < x < 1$), $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (where $0 \leq x \leq 1$ and $0 \leq y \leq 1$).
9. Method according to any one of claims 1 to 8, characterised in that said nanoparticles of a material P comprise nanoparticles composed of a core of material P and a shell.
 10. Method according to claim 9, characterised in that said shell is formed of a material which is an electronic conductor.
 11. Method according to claim 9, characterised in that said shell is formed of a material which is an electronic insulator and a cation conductor, in particular a lithium ion conductor.
 12. Method for manufacturing a lithium ion battery, comprising the steps of the method for manufacturing a dense layer according to any one of claims 1 to 11.
 13. Method according to claim 11, wherein a porous layer intended to form the separator is also deposited.
 14. Method according to claim 13, wherein said porous layer is a mesoporous layer with a mesoporous volume between 25% and 75%, and even more preferably between 30% and 60%.
 15. Method according to any one of claims 13 to 14, wherein the method for depositing said porous layer is a method selected preferably in the group formed by: electrophoresis, a printing method, selected preferably from ink-jet printing and flexographic printing, and a coating method selected preferably from roll coating, curtain coating, doctor blade coating, slot-die coating, dip-coating, knowing that in any case, the deposition is carried out using a suspension of nanoparticle aggregates or agglomerates.

16. Method according to any one of claims 13 to 15, wherein a colloidal suspension is used for depositing said porous layer comprising aggregates or agglomerates of nanoparticles of at least one inorganic material, of mean primary diameter D_{50} between 2 nm and 100 nm, preferably between 2 nm and 60 nm, said aggregates or agglomerates typically having a mean diameter D_{50} between 50 nm and 300 nm, and preferably between 100 nm and 200 nm.
17. Method according to any one of claims 15 to 16, wherein said layer thus obtained is dried and is consolidated, by pressing and/or heating, to obtain a porous layer, preferably mesoporous and inorganic.
18. Method according to any one of claims 13 to 17, wherein said porous layer is deposited on said dense layer.
19. Method according to any one of claims 13 to 17, wherein said dense layer is deposited on said porous layer.
20. Method according to any one of claims 13 to 19, wherein said porous separating layer is impregnated with a mobile lithium ion carrier liquid, which is preferably selected in the group formed by:
 - o an electrolyte composed of at least one aprotic solvent and at least one lithium salt;
 - o an electrolyte composed of at least one ionic liquid or ionic polyliquid and at least one lithium salt;
 - o a mixture of at least one aprotic solvent and at least one ionic liquid or ionic polyliquid and at least one lithium salt;
 - o a polymer rendered an ionic conductor by adding at least one lithium salt; and
 - o a polymer rendered an ionic conductor by adding a liquid electrolyte, either in the polymer phase, or in the mesoporous structure,
 said polymer being preferably selected in the group formed by poly(ethylene oxide), poly(propylene oxide), polydimethylsiloxane, polyacrylonitrile, poly(methyl methacrylate), poly(vinyl chloride), poly(vinylidene fluoride), PVDF-hexafluoropropylene.
21. Dense layer capable of being prepared with the method according to any one of claims 1 to 11.
22. Dense layer according to claim 21, characterised in that it is selected from an anode, a cathode or an electrolyte in an electrochemical device, in particular a lithium ion battery.

23. Electrochemical device, comprising at least one dense layer according to claim 21 or 22.
24. Electrochemical device according to claim 23, characterised in that it consists of a battery with a capacitance not exceeding 1 mA h, and particularly a lithium ion
5 battery.
25. Lithium ion battery according to claim 24, characterised in that it comprises an anode and/or a cathode which are dense layers according to one of claims 21 or 22.
26. Lithium ion battery according to claim 24 or 25, characterised in that it comprises an electrolyte layer which is a dense layer according to one of claims 21 or 22.
- 10 27. Lithium ion battery according to claim 25, characterised in that it comprises a liquid electrolyte infiltrated in a porous separator separating said anode and said cathode.