

METHOD FOR MANUFACTURING A POROUS ELECTRODE, AND MICROBATTERY CONTAINING SUCH AN ELECTRODE

Technical field of the invention

- 5 The invention relates to the field of electrochemistry, and more particularly to thin layer electrochemical systems. It relates more specifically to electrodes that can be used in electrochemical systems such as lithium-ion microbatteries. The invention applies to negative electrodes and positive electrodes. It relates to porous electrodes that can be impregnated with a solid electrolyte without liquid phase or liquid electrolyte.
- 10 The invention also relates to a method for preparing such a porous electrode which implements nanoparticles of an electrode material, and to the electrodes thus obtained. The invention also relates to a method for manufacturing a lithium-ion microbattery comprising at least one of these electrodes, and the microbatteries thus obtained.

15 Prior art

- Lithium-ion batteries have the best energy density among the various electrochemical storage technologies on the market. There are various architectures and chemical electrode compositions to produce these batteries. The methods for manufacturing lithium-ion batteries are presented in many articles and patents; an inventory is given in the book
- 20 "*Advances in Lithium-ion batteries*" (ed. W. van Schalkwijk and B. Scrosati), published in 2002 (Kluwer Academic/Plenum Publishers).

- There is a growing need for microbatteries, that is to say for very small rechargeable batteries, capable of being integrated on electronic cards; these electronic circuits can be used in many fields, for example in cards to secure transactions, in electronic labels, in
- 25 implantable medical devices, in various micromechanical systems.

- According to the prior art, the electrodes of the lithium-ion batteries can be manufactured using coating techniques, in particular by roll coating, doctor blade coating, tape casting, slot-die coating. With these methods an ink consisting of particles of active materials in the form of powder is deposited on the surface of a substrate; the particles constituting this
- 30 powder have an average particle size which is typically between 5 μm and 15 μm in diameter.

- These techniques allow to produce layers of a thickness comprised between approximately 50 μm and approximately 400 μm . The power and energy of the battery can be modulated by adapting the thickness and porosity of the layers, and the size of the active particles that
- 35 constitute them.

Inks (or pastes) deposited to form the electrodes contain active material particles, but also (organic) binders, carbon powder allowing to ensure electrical contact between particles, and solvents that are evaporated during the step of drying the electrodes. To improve the quality of electrical contacts between the particles and to compact the deposited layers, a
 5 calendering step is performed on the electrodes. After this compression step, the active particles of the electrodes occupy about 60% of the volume of the deposition, which means that there is usually about 40% of porosities between the particles.

To best optimise the density of volume energy of lithium-ion microbatteries produced with conventional manufacturing methods, it can be extremely useful to reduce the porosity of
 10 the electrodes; thus, the amount of active ingredient is increased per electrode volume unit. This can be done in many ways.

In the extreme, completely dense layers, devoid of porosity can be used; thus the volume energy density of the electrode is maximum. Such dense layers can be produced using vacuum deposition techniques, for example by Physical Vapour Deposition (abbreviated
 15 PVD). However, since these layers devoid of pores (layers called “fully solid layers”) cannot contain a liquid electrolyte to facilitate the ionic transport or electronic conductive fillers to facilitate the transport of electrical charges, their thickness in a battery must remain limited to a few micrometres, because otherwise they would become too resistive.

It is also possible to optimise conventional inking techniques to increase the density of
 20 layers obtained after calendering. It has been shown that by optimising the size distribution of the deposited particles it is possible to reach a density of the layer of 70% (see the publication of J. Ma and L.C. Lim, “*Effect of particle size distribution of sintering of agglomerate-free submicron alumina powder compacts*”, published in 2002 in J. Europ. Ceramic Soc. 22 (13), p. 2197-2208). It can be estimated that an electrode having 30%
 25 porosity, containing conductive fillers and impregnated with a lithium-ion conductive electrolyte, would have a higher volume energy density of about 35% compared to the same electrode with 50% porosity consisting of particles which are monodisperse in size. Moreover, because of the impregnation by highly ion conductive phases and the addition of electronic conductors, the thickness of these electrodes can be very much increased
 30 compared to what is possible with the techniques of vacuum deposition, which lead to compact but more resistive layers. This increase in the thickness of the electrodes increases the energy density of the battery cells thus obtained.

However, although allowing to increase the energy density of the electrodes, such a size distribution of the active material particles is not without problems. Particles of different sizes
 35 in an electrode will have different capacities. Under the effect of identical charge and/or discharge currents they will be locally more or less charged and/or discharged according to

their size. When the battery will no longer be subjected to current, the local charge states between particles will be balanced again, but during the transient phases, local imbalances can lead to locally stressing the particles outside their stable voltage ranges. These local charge imbalances will be all the more pronounced as the current density will be significant.

5 These imbalances therefore induce a loss of cycling performance, a safety risk and a limitation of the power of the battery cell. The same goes when the electrodes have non-homogenous porosity, namely distributed in size; this non-homogeneity contributes to making the wetting of the pores of the electrodes more difficult.

These effects of the particle size distribution of the active material particles on the
10 current/voltage relationships of the electrodes were studied by numerical simulation in the publication "*A study on the Effect of Porosity and Particle Size Distribution On Li-Ion Battery Performance*" by S.T. Taleghani and al., published in 2017 in the journal *J. Electrochem. Soc.* 164 (11), p. E3179-E3189). According to the prior art, active material particles with a size typically comprised between 5 μm and 15 μm are used with the techniques for inking
15 the electrodes mentioned above. The contact between each of the particles is essentially punctual, and the particles are bound together with an organic binder which is in most cases polyvinylidene fluoride (abbreviated PVDF).

Binder-free mesoporous electrode layers for lithium-ion batteries can be deposited by electrophoresis; this is known from WO 2019/215 407 (I-TEN). They can be impregnated
20 with a liquid electrolyte, but their electrical resistivity remains quite high.

Liquid electrolytes used for impregnating porous electrodes consist of aprotic solvents wherein lithium salts were dissolved. They are very flammable and can give rise to violent combustions of battery cells, especially when the active cathode materials are subjected to voltage ranges outside their stability voltage range, or when hot spots appear locally in the
25 cell.

To find a solution to these safety problems inherent in the structure of lithium-ion battery cells, one can work along three axes.

According to a first axis, the organic solvent-based electrolytes can be replaced by ionic liquids, which are extremely temperature-stable. However, the ionic liquids do not wet the
30 surfaces of the organic materials, and the presence of PVDF and other organic binders in the conventional lithium-ion battery electrodes prevents anchoring electrodes from being wet by this type of electrolyte; the performance of the electrodes is impacted. Ceramic separators have been developed to overcome this problem at the electrolytic junction between electrodes, but the fact remains that the presence of organic binders in the
35 electrodes continues to cause problems for the use of ionic liquid-based electrolytes.

According to a second axis, it can be sought to homogenise particle sizes, in order to avoid local imbalances of charge states that can lead during intensive discharges to locally stress active materials outside their operating voltage ranges. This optimisation would then be at the expense of the energy density of the cell.

- 5 According to a third axis, the distribution and division of conductive fillers (usually carbon black) can be homogenised in the electrode, in order to avoid locally having more electrically resistive areas that could lead to the formation of a hot spot during the battery power operation.

As regards more particularly the methods for manufacturing battery electrodes according to
10 the prior art, their manufacturing cost depends in part on the nature of the solvents and inks used. In addition to the intrinsic cost of the active materials, the cost of manufacturing the electrodes results essentially from the complexity of the inks used (binders, solvents, carbon black). The main solvent used for the production of lithium-ion battery electrodes is N-methyl-2-pyrrolidone (abbreviated NMP). NMP is an excellent solvent for dissolving PVDF
15 which acts as a binder in the formulation of inks.

The drying of the NMP contained in the electrodes is a real economic issue. The high boiling temperature of the NMP coupled to its very low vapour pressure makes its drying difficult to achieve in an industrial environment. Solvent vapours should be collected and reprocessed. Moreover, to ensure better adhesion of the electrodes to the substrates, the drying
20 temperature of the NMP should not be too high, which tends to increase the drying time and its cost once again; this is described in the publication "*Technical and economic analysis of solvent-based lithium-ion electrode drying with water and NMP*" by D.L. Wood & al., published in the journal *Drying Technology*, vol. 36, n°2 (2018).

Other less expensive solvents can be used to produce inks, in particular water and ethanol.
25 However, their surface tension is greater than that of the NMP, and therefore they wet the surface of the metal power collectors less well. In addition, the particles tend to agglomerate in water, especially carbon black nanoparticles. These agglomerations lead to a heterogeneous distribution of the components entering into the composition of the electrode (binders, carbon black...). In addition, whether with water or ethanol, traces of water can
30 remain adsorbed on the surface of the particles of active materials, even after drying.

Finally, in addition to the problems related to the formulation of the inks to obtain a low-cost efficient electrode, it must be borne in mind that the ratio between the energy density and the power density of the electrodes can be adjusted according to the particle size of the active materials, and indirectly to the porosity of the electrode layers and their thickness.
35 The article by J. Newman ("*Optimization of Porosity and Thickness of a Battery Electrode by Means of a Reaction-Zone Model*", *J. Electrochem. Soc.*, 142 (1), p. 97-101 (1995))

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

The problem that the present invention seeks to overcome is to provide a new electrode for lithium-ion microbattery with a very high energy density coupled with a very high power density, which has excellent cycle life as well as an increased safety.

Objects of the invention

More particularly, to overcome these safety problems inherent in the structure of conventional lithium-ion battery cells, the inventors followed three guidelines:

10 According to a first guideline, organic solvent-based electrolytes are replaced by mixtures of organic solvents and ionic liquids or by ionic liquids, which are extremely temperature-stable. However, the ionic liquids do not wet on the surfaces of organic materials and the presence of PVDF and other organic binders in conventional battery electrodes prevents wetting of the electrodes by this type of electrolyte, and the performance of the electrodes
15 is affected. Ceramic separators have been developed to overcome this problem at the electrolytic junction between electrodes, but the fact remains that the presence of organic binders in the electrodes continues to pose problems for the use of electrolytes based on ionic liquids.

According to a second guideline, it is sought to homogenise the sizes of particles, in order
20 to avoid local imbalances of states of charge which can lead during intensive discharges to locally stress active materials outside their conventional operating voltage ranges.

According to a third guideline, it is sought to homogenise the distribution and division of conductive additives ("conductive fillers"; only carbon black is used in practice) in the electrode, in order to avoid locally having more electrically resistive areas that could lead to
25 the formation of a hot spot during the battery power operation.

According to the invention, the problem is solved by a lithium-ion microbattery electrode which is completely ceramic, mesoporous, devoid of organic binders, and the porosity of which is comprised between 50% and 25%, and the size of the channels and pores of which is homogeneous to ensure a perfect dynamic balancing of the cell.

30 This fully solid mesoporous structure, without organic components, is obtained by the deposition, on a substrate, of agglomerates and/or aggregates of nanoparticles of active materials. The sizes of the primary particles constituting these agglomerates and/or aggregates are in the range of the nanometre or tens of nanometres, and the agglomerates and/or aggregates contain at least four primary particles.

Said substrate may be, in a first embodiment, a substrate capable of acting as an electric current collector, or be, in a second embodiment, an intermediate, temporary substrate which will be explained in more detail below.

The fact of using agglomerates of a few tens or even hundreds of nanometres in diameters rather than non-agglomerated primary particles each having a size in the range of the nanometre or tens of nanometres allows to increase the deposition thicknesses. The agglomerates must have a size less than 300 nm. The sintering of agglomerates greater than 500 nm would not allow to obtain a mesoporous continuous film. In this case, two sizes of different porosity are observed in the deposition, namely porosity between agglomerates and porosity inside the agglomerates.

Indeed, it is observed that during drying of the nanoparticle depositions on a substrate capable of acting as an electric current collector, cracks appear in the layer. It can be seen that the appearance of these cracks depends essentially on the size of the particles, the compactness of the deposition and its thickness. This limit thickness of cracking is defined by the following relationship:

$$h_{\max} = 0.41 [(GM\phi_{\text{rcp}}R^3)/2\gamma]$$

where $h_{\max}$ designates the critical thickness, g the nanoparticle shear module, M the number of coordination, ϕ_{rcp} the volume fraction of nanoparticles, R the radius of the particles and γ the interfacial tension between the solvent and the air.

It follows that the use of agglomerates, which are mesoporous, consisting of primary nanoparticles at least ten times smaller than the size of the agglomerate, allows to considerably increase the limit thickness of cracking of the layers. In the same way, it is possible to add a few percent of a solvent with a lower surface tension (such as isopropyl alcohol (abbreviated IPA)) in water or ethanol to improve the wettability and the adhesion of the deposition, and to reduce the risk of cracking. In order to increase the deposition thicknesses while limiting or eliminating the appearance of cracks, it is possible to add binders, dispersants. These additives and organic solvents can be eliminated by heat treatment under air, such as debinding, during a sintering treatment or during a heat treatment carried out prior to the sintering treatment.

Moreover, for the same size of primary particles, it is possible during their synthesis by precipitation to modify the size of the agglomerates by modulating the amount of ligands (for example polyvinyl pyrrolidone, abbreviated PVP) in the synthesis reactor. Thus, it is possible to produce an ink containing agglomerates which are very dispersed in size or having two complementary size populations, so as to maximise the compactness of the deposition of agglomerates. Unlike the sintering of non-agglomerated nanoparticles, the sintering conditions between agglomerates of different sizes will not be changed. These are

the primary nanoparticles, which constitute the agglomerates which will weld together. These primary nanoparticles have identical sizes regardless of the size of the agglomerate. The size distribution of the agglomerates will improve the compactness of the depositions and increase the points of contact between nanoparticles, but will not modify the consolidation temperature.

However, the agglomerates must remain small to be able to form during the heat treatment of the layer a continuous mesoporous film. If the agglomerates are too large, this hinders their sintering and the formation of two distinct porosities is observed in the layer: a porosity between agglomerates and a porosity inside the agglomerates.

After partial sintering, a porous, preferably mesoporous, layer or a plate is obtained, without carbon black or organic binders, wherein all the nanoparticles are welded together (by the necking phenomenon, which is also known) to form a continuous mesoporous network characterised by unimodal porosity. The porous, preferably mesoporous, layer thus obtained is entirely solid and ceramic. There is no longer any risk of loss of electrical contact between the particles of active materials during cycling, which is likely to improve the cycling performance of the battery. Moreover, after sintering, the porous, preferably mesoporous, layer adheres perfectly to the metal substrate on which it has been deposited or transferred (in the case of an initial deposition on an intermediate substrate).

The heat treatments carried out at high temperature to sinter the nanoparticles together allow the electrode to dry perfectly and remove all traces of water or solvents or other organic additives (stabilisers, binders) adsorbed on the surface of the active material particles. The high temperature heat treatment (sintering) can be preceded by a lower temperature heat treatment (debinding) to dry the placed or deposited electrode and to remove traces of water or solvents or other organic additives (stabilisers, binders) adsorbed on the surface of active material particles; this debinding can be carried out in an oxidising atmosphere.

Depending on the sintering times and temperature, it is possible to adjust the porosity of the final electrode. Depending on the energy density requirements, the latter can be adjusted within a range comprised between 50% and 25% porosity.

In all cases, the power density of the electrodes thus obtained remains extremely high due to the mesoporosity. Moreover, independently of the size of the mesopores in the active material (knowing that after sintering the notion of nanoparticle no longer applies to the material which then has a three-dimensional structure with a network of channels and mesopores), the dynamic cell balancing remains perfect, which helps to maximise power densities and battery cell lives.

- The electrode according to the invention has a high specific surface, which reduces the ionic resistance of the electrode. However, for this electrode to deliver maximum power, it must still have very good electronic conductivity to avoid ohmic losses in the battery. This improvement in the electronic conductivity of the cell will be all the more critical the greater the thickness of the electrode. Moreover, this electronic conductivity must be perfectly homogeneous throughout the electrode in order to avoid the local formation of hot spots. According to the invention, a coating of an electronically conductive material is deposited on and inside the pores of the porous layer. This electronically conductive material can be deposited by the Atomic Layer Deposition technique (abbreviated as ALD) or from a liquid precursor. Said electronically conductive material may be carbon.
- To deposit a carbon layer from a liquid precursor, the mesoporous layer can be immersed in a solution which is rich of a carbon precursor (for example, a solution of a carbohydrate, such as sucrose). Then the electrode is dried and subjected to a heat treatment under nitrogen at a temperature sufficient to pyrolyze the carbon precursor. This forms a very thin coating of carbon over the entire internal surface of the electrode, which is perfectly distributed. This coating gives the electrode good electronic conduction, regardless of its thickness. It should be noted that this treatment is possible after sintering because the electrode is entirely solid, without organic residues, and withstands the thermal cycles imposed by the various heat treatments.
- A first object of the invention is a method for manufacturing a porous electrode, in particular for electrochemical devices, said electrode comprising a porous layer deposited on a substrate, said layer being free of binder, having a porosity comprised between 20% and 60% by volume, preferably between 25% and 50%, and pores with an average diameter of less than 50 nm, said manufacturing method being characterised in that:
- (a) provision is made of a substrate and a colloidal suspension or a paste comprising aggregates or agglomerates of monodisperse primary nanoparticles of at least one active electrode material P, having an average primary diameter D_{50} comprised between 2 nm and 150 nm (preferably between 2 nm and 100 nm, preferably between 2 nm and 60 nm and even more preferably between 2 nm and 50 nm), said aggregates or agglomerates having an average diameter D_{50} comprised between 50 nm and 300 nm (preferably between 100 nm to 200 nm),
 - (b) a layer is deposited from said colloidal suspension or paste provided in step (a) on at least one face of said substrate by a method selected from the group formed of: electrophoresis, a printing method, in particular the ink-jet printing method or flexographic printing, a coating method and preferably using a doctor blade, that is to say by doctor blade coating, roll coating, curtain coating, dip-coating or slot-die coating,

- (c) said layer obtained in step (b) is dried, where appropriate before or after having separated said layer from its intermediate substrate, then, optionally, said dried layer is heat treated, preferably under an oxidising atmosphere, and it is consolidated, by pressing and/or heating, to obtain a porous, preferably mesoporous, layer,
- 5 (d) a coating of an electronically conductive material is deposited on and inside the pores of the porous layer,

knowing that said substrate may be a substrate capable of acting as an electric current collector, or an intermediate substrate.

Advantageously, after step d) the electrode obtained can be coated with an ionic conductive layer to improve the life of batteries and their performance. The ionic conductive layer may be $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$, nafion, Li_3BO_3 , PEO, or else a mixture of PEO and a phase carrying lithium ions, such as lithium salts.

In step (b) the deposition may be carried out on one or both faces of the substrate.

Advantageously, when said substrate is an intermediate substrate, said layer is separated in step (c) from said intermediate substrate, to form, after consolidation, a porous plate. This separation step can be carried out before or after drying the layer obtained in step b).

Advantageously, when said substrate is an intermediate substrate, after step c) and before step d), provision is made of an electrically conductive sheet, covered on at least one face, preferably on its two faces, with a thin layer of conductive glue or a thin layer of nanoparticles of at least one active electrode material P, then at least one porous plate is glued on one face, preferably on each of the faces, of the electrically conductive sheet, so as to obtain a porous, preferably mesoporous, layer on a substrate capable of acting as a current collector.

Advantageously, when said colloidal suspension or paste provided in step (a) comprises organic additives, such as ligands, stabilisers, binders or residual organic solvents, said layer dried in step c) is heat treated, preferably under an oxidising atmosphere. This heat treatment, allowing debinding, can be carried out at the same time as the consolidation (sintering) when it is carried out under an oxidising atmosphere or before the step of consolidating the dried layer in step c).

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In a first embodiment, said substrate is a substrate capable of acting as electric current collector. Its chemical nature must be compatible with the temperature of the heat treatment of step (c) of the method for manufacturing the porous electrode (debinding and/or sintering heat treatments); in particular, it must not melt or form an oxide layer that would have too high electrical resistance, or react with electrode materials. Advantageously, a metal substrate is selected, which can in particular be made of tungsten, molybdenum, chromium,

titanium, tantalum, stainless steel, or an alloy of two or more of these materials. Such metal substrates are quite expensive and can greatly increase the cost of the battery. This metal substrate can also be coated with a conductive or semiconductor oxide before depositing the layer of material P. The thickness of the layer after step (c) is advantageously comprised
 5 between approximately 1 μm and approximately 300 μm , preferably between 1 μm and 150 μm , more preferably between 10 μm and 50 μm , or else between 10 μm and 30 μm . When the substrate used is a substrate capable of acting as an electric current collector, the thickness of the layer after step (c) is limited in order to avoid any cracking problem.

10 In a second embodiment, said substrate is an intermediate, temporary substrate, such as a flexible substrate, which may be a polymer film. In this second embodiment, the deposition step is advantageously carried out on one face of said intermediate substrate in order to facilitate the subsequent separation of the layer from its substrate. In this second embodiment, the layer can be separated from its substrate after drying, preferably before
 15 heating it, but at the latest at the end of step (c). The thickness of the layer after step (c) is advantageously less than or equal to 5 mm, advantageously comprised between approximately 1 μm and approximately 500 μm . The thickness of the layer after step (c) is advantageously less than 300 μm , preferably, comprised between approximately 5 μm and approximately 300 μm , preferably between 5 μm and 150 μm .

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Advantageously, said porous layer obtained at the end of step (c) has a specific surface comprised between 10 m^2/g and 500 m^2/g . Its thickness is advantageously comprised between 1 and 500 μm , preferably comprised between 4 and 400 μm .

The size distribution of the primary particles of the active material P is preferably narrow. In
 25 a preferred manner, said agglomerates preferably comprise at least three primary particles. The size distribution of said agglomerates is preferably polydisperse. In one embodiment, the distribution of the agglomerate size is bimodal, that is to say that it has two size distribution peaks, these two sizes being called D1 and D2 where $D1 > D2$; the ratio $D2/D1$ may be comprised for example between 3 and 7 and preferably between 4 and 6; this avoids
 30 the formation of large cavities and ensures a good compactness of the mesoporous layer. The suspension of nanoparticles can be produced in water or in ethanol, or in a mixture of water and ethanol, or alternatively in a mixture of ethanol and isopropyl alcohol (with less than 3% of isopropyl alcohol). It does not contain carbon black.

To use coating techniques, such as roll coating, curtain coating, slot-die coating or dip-
 35 coating, the suspension used is advantageously characterised by a dry extract of at least 15% and preferably at least 50%.

The deposition of said coating of electronically conductive material can be carried out by the atomic layer deposition ALD technique, or by immersion of the porous layer in a liquid phase including a precursor of said electronically conductive material, followed by the transformation of said precursor into electronically conductive material.

- 5 Said precursor is advantageously a carbon-rich compound, such as a carbohydrate, preferably a polysaccharide, and said transformation into an electronically conductive material is in this case carried out by pyrolysis, preferably under an inert atmosphere (for example nitrogen). Said electronically conductive material may be carbon. It can be deposited in particular by ALD or by immersion into a liquid phase including a carbon
10 precursor.

In said second embodiment, the method for manufacturing the battery porous electrode uses an intermediate polymer substrate (such as the PET) and results in a tape called "raw tape". This tape is then separated from its substrate; then it forms plates or sheets (hereinafter the term "plate" is used, regardless of its thickness). After cutting, these plates
15 can be separated from their intermediate substrate. These plates are then calcined in order to remove the organic constituents. These plates are then sintered in order to consolidate the nanoparticles until a mesoporous ceramic structure is obtained with a porosity comprised between 25 and 50%. Said porous plate obtained in step (c) has a thickness advantageously less than or equal to 5 mm, preferably comprised between approximately
20 1 μm and approximately 500 μm . The thickness of the layer after step (c) is advantageously less than 300 μm , preferably, comprised between approximately 5 μm and approximately 300 μm , preferably between 5 μm and 150 μm . A coating of an electronically conductive material is then deposited on and inside the pores of the porous layer or porous plate, which is preferably mesoporous, as just described.

25 In this second embodiment, provision is also made of an electrically conductive sheet, covered on both faces with a thin intermediate layer of nanoparticles preferably identical to those constituting the electrode plate or covered on both faces with a thin layer of conductive glue. Said thin layers preferably have a thickness of less than 1 μm . This sheet can be a
30 metal strip or a graphite sheet.

This electrically conductive sheet is then interposed between two plates of porous electrodes obtained previously, respectively between two porous plates obtained after step c). The assembly is then heat-pressed so that said intermediate nanoparticle thin layer is
35 transformed by sintering and consolidates the electrode/substrate/electrode assembly, respectively the porous plate/substrate/porous plate assembly to obtain a rigid and integral

sub-assembly. During this sintering, the bond between the electrode layer, respectively the porous plate, and the intermediate layer is established by atom diffusion; this phenomenon is known by “diffusion bonding”. This assembly is produced with two electrode plates, respectively two porous plates, of the same polarity (typically between two anodes or
5 between two cathodes), and the metal sheet between these two electrode plates, respectively two porous plates, of the same polarity establishes a parallel connection therebetween.

One of the advantages of the second embodiment is that it allows the use of inexpensive substrates such as aluminium strips, copper or graphite strips. Indeed, these strips would
10 not withstand the heat treatments for consolidating the deposited layers; gluing them to the electrode plates after their heat treatment also helps prevent their oxidation.

According to another variant of the second embodiment, when a porous plate/substrate/porous plate assembly is obtained, the coating of an electronically conductive material can then advantageously be deposited on and inside the pores of the
15 porous, preferably mesoporous, plates, of the porous plate/substrate/porous plate assembly, as has been described previously, in particular when the used porous plates are thick.

The deposition of said coating of electronically conductive material can be carried out by the atomic layer deposition ALD technique, or by immersion of the porous layer into a liquid
20 phase including a precursor of said electronically conductive material, followed by the transformation of said precursor into an electronically conductive material.

This “diffusion bonding” assembly can be carried out separately as has just been described, and the electrode/substrate/electrode sub-assemblies thus obtained can be used to manufacture a battery. This diffusion bonding assembly can also be achieved by stacking
25 and heat-pressing the entire battery structure; in this case, a multilayer stack comprising a first porous anode layer, its metallic substrate, a second porous anode layer, a solid electrolyte layer, a first cathode layer, its metallic substrate, a second cathode layer, a new solid electrolyte layer, and so on, is assembled.

More specifically, electrode plates, which are mesoporous ceramic can either be glued on
30 both faces of a metal substrate (then the same configuration as that resulting from the depositions on both faces of a metal substrate is found).

This electrode/substrate/electrode sub-assembly can be obtained by gluing the electrode plates to an electrically conductive sheet capable of subsequently acting as an electric current collector, or by depositing then sintering layers on a substrate capable of acting as
35 an electric current collector, in particular a metal substrate.

Regardless of the embodiment of the electrode/substrate/electrode sub-assembly, the electrolyte film (separator) is then deposited on the latter. The necessary cuts are then made to produce a battery with several elementary cells, then the sub-assemblies are stacked (typically in “head to tail” mode) and the thermocompression is carried out to weld the electrodes together at the solid electrolyte.

Alternatively, the necessary cuts to produce a battery with several elementary cells can be made before the deposition on each electrode/substrate/electrode sub-assembly of an electrolyte film (separator), then the sub-assemblies are stacked (typically in “head to tail” mode) and the thermocompression is carried out to weld the electrodes together at the electrolyte film (separator).

In the two variants which have just been presented, the thermocompression welding takes place at a relatively low temperature, which is possible thanks to the very small size of the nanoparticles. As a result, oxidation of the metal layers of the substrate is not observed.

In other embodiments of the assembly, which will be described below, use is made of a conductive glue (loaded with graphite) or a sol-gel-type deposition loaded with conductive particles, or else metal strips, preferably having a low melting point (for example aluminium); during thermomechanical (heat pressing) treatment the metal strip can be deformed by creep and achieve this weld between the plates.

If the electrode should be used in a battery, an active material P which is dimensionally stable during the charge and discharge cycles is preferably selected. It may be particularly selected from the group formed of:

- o the oxides LiMn_2O_4 , $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ with $0 < x < 0.15$, 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 $0 < x < 0.1$, $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ with 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 , $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ with $0 \leq x < 0.15$, $\text{LiNi}_{1/x}\text{Co}_{1/y}\text{Mn}_{1/z}\text{O}_2$ with $x+y+z=10$;
- o $\text{Li}_x\text{M}_y\text{O}_2$ where $0.6 \leq y \leq 0.85$; $0 \leq x+y \leq 2$; and M is selected from Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Sn, and Sb or a mixture of these elements; $\text{Li}_{1.20}\text{Nb}_{0.20}\text{Mn}_{0.60}\text{O}_2$;
- o $\text{Li}_{1+x}\text{Nb}_y\text{Me}_z\text{A}_p\text{O}_2$ where Me is at least one transition metal selected from: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re,

Os, Ir, Pt, Au, Hg, Rf, Db, Sg, Bh, Hs and Mt, and where $0.6 < x < 1$; $0 < y < 0.5$; $0.25 \leq z < 1$; with $A \neq \text{Me}$ and $A \neq \text{Nb}$, and $0 \leq p \leq 0.2$;

- o $\text{Li}_x\text{Nb}_{y-a}\text{Na}_a\text{M}_{z-b}\text{P}_b\text{O}_{2-c}\text{F}_c$ where $1.2 < x \leq 1.75$; $0 \leq y < 0.55$; $0.1 < z < 1$; $0 \leq a < 0.5$; $0 \leq b < 1$; $0 \leq c < 0.8$; and where M, N, and P are each at least one of the elements selected from the group consisting of Ti, Ta, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Zr, Y, Mo, Ru, Rh, and Sb;
- o $\text{Li}_{1.25}\text{Nb}_{0.25}\text{Mn}_{0.50}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.40}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Fe}_{0.40}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.43}\text{Ni}_{0.27}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.43}\text{Co}_{0.27}\text{O}_2$; $\text{Li}_{1.4}\text{Nb}_{0.2}\text{Mn}_{0.53}\text{O}_2$;
- o $\text{Li}_x\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_y$ where $0.00 \leq x \leq 1.52$; $1.07 \leq y < 2.4$; $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$;
- o $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ where $0 \leq x$ and $y \leq 0.5$; $\text{LiNi}_x\text{Ce}_z\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ where $0 \leq x$ and $y \leq 0.5$ and $0 \leq z$;
- o phosphates LiFePO_4 , LiMnPO_4 , LiCoPO_4 , LiNiPO_4 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; $\text{Li}_2\text{MPO}_4\text{F}$ with $\text{M} = \text{Fe, Co, Ni}$ or a mixture of these different elements, LiMPO_4F with $\text{M} = \text{V, Fe, T}$ or a mixture of these different elements; the phosphates of formula $\text{LiMM}'\text{PO}_4$, with M and M' ($\text{M} \neq \text{M}'$) selected from Fe, Mn, Ni, Co, V such as the $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ and where $0 < x < 1$;
- o oxyfluorides of the type $\text{Fe}_{0.9}\text{Co}_{0.1}\text{OF}$; LiMSO_4F with $\text{M} = \text{Fe, Co, Ni, Mn, Zn, Mg}$;
- o all lithiated forms of the following chalcogenides: V_2O_5 , V_3O_8 , TiS_2 , titanium oxysulfides (TiO_yS_z with $z=2-y$ and $0.3 \leq y \leq 1$), tungsten oxysulfides (WO_yS_z with $0.6 < y < 3$ and $0.1 < z < 2$), CuS , CuS_2 , preferably $\text{Li}_x\text{V}_2\text{O}_5$ with $0 < x \leq 2$, $\text{Li}_x\text{V}_3\text{O}_8$ with $0 < x \leq 1.7$, Li_xTiS_2 with $0 < x \leq 1$, titanium and lithium oxysulfides with $\text{Li}_x\text{TiO}_y\text{S}_z$ with $z=2-y$, $0.3 \leq y \leq 1$ and $0 < x \leq 1$, $\text{Li}_x\text{WO}_y\text{S}_z$ with $z=2-y$, $0.3 \leq y \leq 1$ and $0 < x \leq 1$, Li_xCuS with $0 < x \leq 1$, Li_xCuS_2 with $0 < x \leq 1$.

A porous layer according to the invention, made with one of these materials, can ensure the cathode function in a battery, and in particular in a lithium-ion battery.

Said material P can also be selected from the group formed of:

- o $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_4\text{Ti}_{5-x}\text{M}_x\text{O}_{12}$ with $\text{M} = \text{V, Zr, Hf, Nb, Ta}$ and $0 \leq x \leq 0.25$;
- o niobium oxides and mixed niobium oxides with titanium, germanium, cerium or tungsten, and preferably from the group formed of:
 - o $\text{Nb}_2\text{O}_{5\pm\delta}$, $\text{Nb}_{18}\text{W}_{16}\text{O}_{93\pm\delta}$, $\text{Nb}_{16}\text{W}_5\text{O}_{55\pm\delta}$ with $0 \leq x < 1$ and $0 \leq \delta \leq 2$, LiNbO_3 ;
 - o $\text{TiNb}_2\text{O}_{7\pm\delta}$, $\text{Li}_w\text{TiNb}_2\text{O}_7$ with $w \geq 0$, $\text{Ti}_{1-x}\text{M}^1_x\text{Nb}_{2-y}\text{M}^2_y\text{O}_{7\pm\delta}$ or $\text{Li}_w\text{Ti}_{1-x}\text{M}^1_x\text{Nb}_{2-y}\text{M}^2_y\text{O}_{7\pm\delta}$ wherein M^1 and M^2 are each at least one element selected from 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^1 and M^2 can be identical or different from each other, and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $0 \leq \delta \leq 0.3$;
 - o $\text{La}_x\text{Ti}_{1-2x}\text{Nb}_{2+x}\text{O}_7$ where $0 < x < 0.5$;

- o $M_xTi_{1-2x}Nb_{2+x}O_{7\pm\delta}$
 - o wherein M is an element whose degree of oxidation is +III, more particularly M is at least one of the elements selected from the group consisting of Fe, Ga, Mo, Al, B, and where $0 < x \leq 0.20$ and $-0.3 \leq \delta \leq 0.3$;
- 5 $Ga_{0.10}Ti_{0.80}Nb_{2.10}O_7$; $Fe_{0.10}Ti_{0.80}Nb_{2.10}O_7$;
- o $M_xTi_{2-2x}Nb_{10+x}O_{29\pm\delta}$
 - o wherein M is an element whose degree of oxidation is +III, more particularly M is at least one of the elements selected from the group consisting of Fe, Ga, Mo, Al, B, and where $0 < x \leq 0.40$ and $-0.3 \leq \delta \leq 0.3$;
- 10 o $Ti_{1-x}M^1_xNb_{2-y}M^2_yO_{7-z}M^3_z$ or $Li_wTi_{1-x}M^1_xNb_{2-y}M^2_yO_{7-z}M^3_z$ wherein
 - o M^1 and M^2 are each at least one element selected from 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,
 - o M^1 and M^2 can be identical or different from each other,
 - 15 o M^3 is at least one halogen,
 - o and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
- o $TiNb_2O_{7-z}M^3_z$ or $Li_wTiNb_2O_{7-z}M^3_z$ wherein M^3 is at least one halogen, preferably selected from F, Cl, Br, I or a mixture thereof, and $0 < z \leq 0.3$;
- o $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7\pm z}$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7\pm z}$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7\pm z}$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7\pm z}$ wherein
 20 x
 - o M^1 is at least one element selected from 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;
 - o $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
- 25 o $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$, wherein
 - o M^1 and M^2 are each at least one element selected from 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, Ce and Sn,
 - 30 o M^1 and M^2 can be identical or different from each other,
 - o and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
- o TiO_2 ;
- o $LiSiTON$.

The nanoparticles used in the present invention may have a core-shell type structure, and in this case said material P forms the core. The shell can be a dielectric material which is an ionic conductor or not.

A porous layer according to the invention, made with one of these materials, can ensure the anode function in a battery, and in particular in a lithium-ion battery. For use as an anode in a lithium-ion battery, an anode material is advantageously used which has a lithium insertion potential greater than 1 V; this allows a very fast recharging of the battery.

- 5 The negative electrode can be made of titanate and/or mixed titanium oxides. Preferably, the electrodes are impregnated with an ionic liquid containing a lithium salt. When said ionic liquid includes sulphur atoms, the substrate capable of acting as electric current collector is, preferably, a noble metal. Such a battery has the advantage of being able to operate at high temperature.
- 10 Another object of the present invention is a porous electrode that can be obtained by the method for manufacturing a porous electrode according to the invention. This porous electrode is free of binder. Its porosity is preferably comprised between 20% and 60% by volume, and the average diameter of its pores is less than 50 nm. It may be intended to act as a positive electrode or as a negative electrode in an electrochemical device.
- 15 An electrode according to the invention allows to produce a lithium-ion microbattery which has both a high energy density and a high power density. This performance is the resultant of a limited porosity (which increases the energy density), of a very high specific surface (which is favoured by the very small size of the primary particles of the electrode, and which leads to increasing the exchange surface, which decreases the ion resistance), of the
20 absence of organic binder (the binder can locally hide lithium access to the surface of the active materials). According to an essential feature of the invention, a coating of an electronically conductive material is deposited on and inside the pores of the porous layer. This coating decreases the series resistance of the battery.
- Still another object of the invention is the use of a porous electrode manufacturing method
25 according to the invention for the manufacture of porous electrodes in lithium-ion batteries. Still another object of the invention is a method for manufacturing a battery designed to have a capacity not exceeding 1 mAh, implementing the method for manufacturing a porous electrode according to the invention, or implementing a porous electrode according to the invention. Said battery is advantageously a lithium-ion battery. In particular, this method for
30 manufacturing a porous electrode can be implemented to manufacture a cathode, and/or to manufacture an anode. This method for manufacturing a battery may comprise a step wherein said porous electrode is impregnated with an electrolyte, preferably a phase carrying lithium ions selected from the group formed of:

- o an electrolyte composed of at least one aprotic solvent and at least one lithium salt;
- 35 o an electrolyte composed of at least one ionic liquid and at least one lithium salt;

- o a mixture of at least one aprotic solvent and at least one ionic liquid and at least one lithium salt;
 - o a polymer made ionically conductive by adding at least one lithium salt; and
 - o a polymer made ionically conductive by adding a liquid electrolyte, either in the
- 5 polymer phase or in the mesoporous structure,

As mentioned above, an electrode according to the invention allows to produce a lithium-ion battery which has both a high energy density and a high power density. Such a battery is also very reliable. There is no risk of loss of electrical contact between particles, which gives them excellent cycling life. Furthermore, the current is perfectly distributed in the

10 electrode, resulting from the homogeneity of the pore size and the local thickness of the active material, which generates a great homogeneity of the electrical conductivity.

The battery according to the invention can in particular be designed and dimensioned so as to have a capacity less than or equal to about 1 mAh (commonly called "microbattery"). Typically, microbatteries are designed to be compatible with microelectronics

15 manufacturing methods.

Thus, a last object of the invention is a lithium-ion microbattery that can be obtained by the method for manufacturing a battery according to the invention.

Figures

20 Figures 1 to 6 illustrate various aspects and embodiments of the invention, without limiting its scope.

[Fig. 1] shows a diffractogram of primary nanoparticles used in the suspension before the formation of agglomerates.

[Fig. 2] shows a picture obtained by transmission electron microscopy of primary

25 nanoparticles of the same sample as that of Figure 1.

[Fig. 3] schematically illustrates nanoparticles before heat treatment.

[Fig. 4] schematically illustrates nanoparticles after heat treatment, illustrating the phenomenon of "necking".

[Fig. 5] shows the evolution of the relative capacity of a battery according to the invention

30 depending on the number of charge and discharge cycles.

[Fig. 6] shows a charging curve of the same battery: the curve A corresponds to the state of charge (right scale), the curve B corresponds to the current absorbed (left scale).

Detailed description

1. Definitions

As part of this document, the size of a particle is defined by its largest dimension. "Nanoparticle" means any particle or object of nanometric size having at least one of its dimensions less than or equal to 100 nm.

"Ionic liquid" means any liquid salt, capable of transporting electricity, being different from
5 all the melted salts by a melting temperature below 100°C. Some of these salts remain liquid at room temperature and do not solidify, even at very low temperature. Such salts are called "ionic liquids at room temperature".

"Mesoporous" materials mean any solid that has within its structure pores called "mesopores" having an intermediate size between that of the micropores (width less than 2
10 nm) and that of the macropores (width greater than 50 nm), namely a size comprised between 2 nm and 50 nm. This terminology corresponds to that adopted by IUPAC (International Union for Pure and Applied Chemistry), which serves as a reference for the person skilled in the art. The term "nanopore" is therefore not used here, even if the mesopores as defined above have nanoscale dimensions within the meaning of the
15 definition of the nanoparticles, knowing that the pores with a size smaller than that of the mesopores are called by the person skilled in the art "micropores".

A presentation of the concepts of porosity (and the terminology that has just been exposed above) is given in the article "*Texture des matériaux pulvérulents ou poreux*" by F. Rouquercol and al., published in the collection "*Techniques de l'Ingénieur*", treaty of
20 Analysis and Characterisation, fascicle P 1050; this article also describes the techniques for characterising porosity, in particular the BET method.

Within the meaning of the present invention, "mesoporous electrode" or "mesoporous layer" means an electrode, respectively a layer which has mesopores. As will be explained below, in these electrodes or layers the mesopores contribute significantly to the total porous
25 volume; this fact is translated by the term "mesoporous electrode or layer of mesoporous porosity greater than X% by volume" used in the description below.

The term "aggregate" means, according to the definitions of IUPAC a weakly bound assembly of primary particles. In this case, these primary particles are nanoparticles having a diameter that can be determined by transmission electron microscopy. An aggregate of
30 aggregated primary nanoparticles can normally be destroyed (that is to say reduced to primary nanoparticles) to make the primary nanoparticles suspended in a liquid phase under the effect of ultrasound, according to a technique known to the person skilled in the art.

The term "agglomerate" means, according to the definitions of IUPAC, a strongly bound assembly of primary particles or aggregates.

The term “microbattery” is used here for a battery of a capacity not exceeding 1 mAh. Typically, microbatteries are designed to be compatible with microelectronics manufacturing methods.

5 2. Preparation of suspensions of nanoparticles

The method for preparing porous electrodes according to the invention starts from a suspension of nanoparticles. It is preferable not to prepare these suspensions of nanoparticles from dry nanopowders. They can be prepared by grinding powders or nanopowders in the liquid phase, and/or using ultrasonic treatment to deagglomerate
10 nanoparticles.

In another embodiment of the invention the nanoparticles are prepared in suspension directly by precipitation. The synthesis of nanoparticles by precipitation allows to obtain primary nanoparticles of very homogeneous size with a unimodal size distribution that is to say a very tight and monodisperse distribution, of good crystallinity and purity. The use of
15 these very homogeneous nanoparticles and narrow distribution allows to obtain a porous structure of controlled and open porosity after deposition. The porous structure obtained after deposition of these nanoparticles has little, preferably no closed pores.

In an even more preferred embodiment of the invention the nanoparticles are prepared directly at their primary size by hydrothermal or solvothermal synthesis; this technique
20 allows to obtain nanoparticles with a very narrow size distribution called “monodisperse nanoparticles”. The size of these non-aggregated or non-agglomerated nanopowders/nanoparticles is called primary size. It is typically comprised between 2 nm and 150 nm. It is advantageously comprised between 10 nm and 50 nm, preferably between 10 nm and 30 nm; this promotes in subsequent method steps the formation of an
25 interconnected mesoporous network with electronic and ionic conduction, thanks to the phenomenon of “necking”.

In an advantageous embodiment, the suspension of monodisperse nanoparticles can be carried out in the presence of ligands or organic stabilisers so as to avoid aggregation, or even the agglomeration of nanoparticles. Binders may also be added in the suspension of
30 nanoparticles to facilitate the production of depositions or raw tapes, in particular thick depositions without cracks.

Indeed, in the context of the present invention, it proves to be preferable to start from a suspension of non-agglomerated primary particles, within which the agglomeration is then induced or caused, rather than allowing the agglomeration of the primary particles to occur
35 spontaneously at the stage of preparation of the suspension.

This suspension of monodisperse nanoparticles can be purified to remove any potentially interfering ions. Depending on the degree of purification it can then be specially treated to form aggregates or agglomerates of a controlled size. More specifically, the formation of aggregates or agglomerates can result from the destabilisation of the suspension caused
5 in particular by ions, by the increase in the dry extract of the suspension, by changing the solvent of the suspension, by the addition of a destabilising agent. If the suspension has been completely purified it is stable, and ions are added to destabilise it, typically in the form of a salt; these ions are preferably lithium ions (preferably added in the form of LiOH).

If the suspension has not been completely purified the formation of aggregates or
10 agglomerates can be done alone in a spontaneous way or by ageing. This way of proceeding is simpler because it involves fewer purification steps, but it is more difficult to control the size of aggregates or agglomerates. One of the essential aspects for the manufacture of electrodes according to the invention consists in properly controlling the size of the primary particles of electrode materials and their degree of aggregation or
15 agglomeration.

If the stabilisation of the suspension of nanoparticles occurs after the formation of agglomerates, they will remain in the form of agglomerates; the suspension obtained can be used to make mesoporous depositions.

It is this suspension of aggregates or agglomerates of nanoparticles which is then used to
20 deposit by electrophoresis, by the ink-jet printing method, by flexographic printing, by doctor blade coating, by roll coating, by curtain coating, by extrusion slot-die coating, or by dip-coating the porous, preferably mesoporous, electrode layers, according to the invention.

According to the observations of the applicant, with an average diameter of the aggregates or agglomerates of nanoparticles comprised between 80 nm and 300 nm (preferably
25 between 100 nm to 200 nm), a mesoporous layer having an average diameter of mesopores comprised between 2 nm and 50 nm is obtained during the subsequent steps of the method. According to the invention, the porous electrode layer can be deposited by the ink-jet printing method or by a coating method, and in particular by the dip-coating method, by roll coating, by curtain coating, by slot-die coating, or else by doctor blade coating, from a fairly
30 concentrated suspension comprising nanoparticle aggregates or agglomerates of the active material P.

It is also possible to deposit the porous electrode layer by electrophoresis, but then advantageously use is made of a less concentrated suspension containing nanoparticle agglomerates of the active material P.

35 The methods for depositing aggregates or agglomerates of nanoparticles by electrophoresis, by the dip-coating method, by ink-jet, by roll coating, by curtain coating, by

slot-die coating or by doctor blade coating are methods which are simple, safe that easy to implement and to industrialise and which allow to obtain a final homogeneous porous layer. Electrophoretic deposition enables uniform deposition of layers over large areas with high deposition rates. The coating techniques, in particular those mentioned above, allow to
 5 simplify the management of the baths compared to the electrophoretic deposition techniques because the suspension does not become depleted of particles during the deposition. Ink-jet printing deposition allows for localised depositions.

Porous layers made of a thick layer can be made in one step by roll coating, curtain coating, slot die coating, or by doctor blade coating (that is to say using a doctor blade).

10 It is noted that colloidal suspensions in water and/or ethanol and/or IPA and mixtures thereof are more fluid than those obtained in the NMP. It is thus possible to increase the dry extract of the suspension of nanoparticle agglomerates. These agglomerates preferably have sizes of less than or equal to 200 nm and have polydisperse sizes, even with two populations with different sizes.

15 Compared to the prior art, the formulation of inks and pastes for the production of the electrodes is simplified. There is no more risk of carbon black agglomerates in the suspension when increasing dry extract.

3. Deposition of layers and their consolidation

In general, a layer of a suspension of nanoparticles is deposited on a substrate, by any
 20 appropriate technique, and in particular by a method selected from the group formed of: electrophoresis, a printing method and preferably ink-jet printing or flexographic printing, a coating method and preferably doctor blade coating, roll coating, curtain coating, dip-coating, or slot-die coating. The suspension is typically in the form of an ink, that is to say a fairly fluid liquid, but can also have a pasty consistency. The deposition technique and the
 25 implementation of the deposition method must be compatible with the viscosity of the suspension, and vice versa.

The deposited layer will then be dried. The layer is then consolidated to obtain the desired mesoporous ceramic structure. This consolidation will be described below. It can be performed by heat treatment, by a heat treatment preceded by a mechanical treatment, and
 30 optionally by a thermomechanical treatment, typically a thermocompression. During this thermomechanical or heat treatment, the electrode layer will be freed of any organic constituent and organic residue (such as the liquid phase of the suspension of the nanoparticles and any surfactant products): it becomes an inorganic layer (ceramic). The consolidation of a plate is preferably carried out after its separation from its intermediate
 35 substrate, since the latter would risk being degraded during this treatment.

The deposition of the layers, their drying and their consolidation are likely to raise some problems which will be discussed now. These problems are partly linked to the fact that during the consolidation of the layers a shrinkage occurs which generates internal stresses.

5 3.1. Substrate capable of acting as a current collector

According to a first embodiment, the layers of electrodes are each deposited on a substrate capable of acting as an electric current collector. Layers including the suspension of nanoparticles or agglomerates of nanoparticles can be deposited on one face or on both faces, by the deposition techniques indicated above. The substrate serving as a current collector within batteries using porous electrodes according to the invention can be metallic, for example a metal strip (that is to say a laminated metal sheet). The substrate is preferably selected from strips of tungsten, molybdenum, chromium, titanium, tantalum, stainless steel, or an alloy of two or more of these materials. Less noble substrates such as copper or nickel may receive a conductive and protective coating against oxidation.

15 The metal sheet can be coated with a noble metal layer, in particular selected from gold, platinum, palladium, titanium or alloys containing mainly at least one or more of these metals, or a layer of ITO type conductive material (which has the advantage of acting as a diffusion barrier).

In general, this substrate capable of acting as an electric current collector must withstand the conditions of heat treatment of the deposited layer, and the operating conditions within the battery cell. As such, copper and nickel are suitable in contact with the cathode material; they may oxidise the anode.

Regarding the deposition of the layers, the electrophoresis method (especially in water) can be used. In this particular case, the substrate is subjected to an electrochemical polarisation which leads either to its oxidation or to its dissolution in the suspension of nanoparticles. In this case, only substrates which do not have anodisation and/or corrosion phenomena can be used. This is in particular the case with stainless steel and noble metals.

When the deposition of nanoparticles and/or agglomerates is carried out by one of the other techniques mentioned below (such as coating, printing) then it is possible to broaden the choice of substrates. This choice will then be made rather depending on the stability of the metal at the operating potential of the electrodes which are associated therewith and upon contact with the electrolytes. However, depending on the synthetic route used to produce the nanoparticles, more or less aggressive heat treatments must be carried out for the consolidation and possible recrystallisation of the nanopowders: this aspect will be further explored in section 5 below.

In all cases, a consolidation heat treatment is necessary to obtain these mesoporous electrodes. It is essential that the substrate capable of acting as an electric current collector can withstand these heat treatments without being oxidised. Several strategies can be used. When the nanopowders deposited on the substrate by inking are amorphous and/or with numerous point defects, it is necessary to carry out a heat treatment which, in addition to consolidation, will also allow to recrystallise the material in the correct crystalline phase with the correct stoichiometry. For this purpose, it is generally necessary to carry out heat treatments at temperatures between 500 and 700°C. The substrate will then have to withstand this type of heat treatment, and it is necessary to use materials that withstand these high temperature treatments. Strips of stainless steel, titanium, molybdenum, tungsten, tantalum, chromium, as well as their alloys can for example be used.

When the nanopowders and/or agglomerates are crystallised, obtained by hydrothermal or solvothermal synthesis with the correct phase and crystalline structure, then it is possible to use consolidation heat treatments under a controlled atmosphere, which will allow to use less noble substrates such as nickel, copper, aluminium, and due to the very small size of the primary particles obtained by hydrothermal synthesis, it is also possible to reduce the temperature and/or the duration of the consolidation heat treatment to values close to 350 - 500°C, which also allows a wider choice of substrates. However, these less noble substrates must withstand the heat treatment allowing to remove the organic additives possibly contained in the suspension of nanoparticles used such as ligands, stabilisers, binders or residual organic solvents (debinding), this heat treatment being advantageously carried out under an oxidising atmosphere.

It is also possible that pseudo-hydrothermal syntheses result in amorphous nanoparticles which will need to be recrystallised later. These substrates capable of acting as an electric current collector can optionally be covered with a thin film of conductive oxide. This oxide may have the same composition as the electrode. These thin films can be produced by sol-gel. This oxide-based interface allows to limit the corrosion of the substrate and ensures a better attachment base for the electrode with the substrate.

With regard to the operating conditions within the battery cell, it should be noted first of all that in the batteries using porous electrodes according to the invention, the liquid electrolytes which impregnate the porous electrode are in direct contact with the substrate capable of acting as a current collector. However, when these electrolytes are in contact with substrates capable of acting as a current collector, that is to say substrates which are metallic and polarised at potentials which are very anodic for the cathode and very cathodic for the anode, these electrolytes are capable of inducing a dissolution of the current

collector. These parasitic reactions can degrade the battery life and accelerate its self-discharge. To avoid this, substrates capable of acting as a current collector such as aluminium current collectors are used at the cathode in all lithium-ion batteries. Aluminium has this peculiarity of being anodised at very anodic potentials, and the oxide layer thus

5 formed at its surface protects it from the dissolution. However, aluminium has a melting temperature close to 600°C and cannot be used for the manufacture of batteries according to the invention, if the electrode consolidation treatments may melt the current collector. Thus, to avoid parasitic reactions that can degrade the life of the battery and accelerate its self-discharge, a titanium strip is advantageously used as a current collector at the cathode.

10 When operating the battery, the titanium strip, such as aluminium, will be anodised and its oxide layer will prevent any parasitic reactions of titanium dissolution in contact with the liquid electrolyte. In addition, as titanium has a much higher melting point than aluminium, fully solid electrodes according to the invention can be made directly on this type of strip. The use of these massive materials, in particular titanium, copper or nickel strips, also

15 allows to protect the cutting edges of the battery electrodes from corrosion phenomena. Stainless steel can also be used as a current collector, especially when containing titanium or aluminium as an alloy element, or when it has a thin layer of protective oxide. Other substrates serving as a current collector can be used such as less noble metal strips covered with a protective coating, allowing to avoid the possible dissolution of these strips

20 induced by the presence of electrolytes to their contact. These less noble metal strips can be Copper, Nickel or metal alloy strips such as stainless steel strips, Fe-Ni alloy, Be-Ni-Cr alloy, Ni-Cr alloy or Ni-Ti alloy strips. The coating that can be used to protect the substrates serving as current collectors may be of different natures. It may be:

25

- a thin layer obtained by the sol-gel method of the same material as that of the electrode. The absence of porosity in this film allows to prevent contacts between the electrolyte and the metal current collector;
- a thin layer obtained by vacuum deposition, in particular by Physical Vapour Deposition (abbreviated PVD) or by Chemical Vapour Deposition (abbreviated

30 CVD), of the same material as that of the electrode;

- a thin metal layer, which is dense, flawless, such as a thin metal layer of gold, titanium, platinum, palladium, tungsten or molybdenum. These metals can be used to protect current collectors as they have good conduction properties and can withstand heat treatments during the subsequent electrode manufacturing method.

35 This layer can in particular be produced by electrochemistry, PVD, CVD, evaporation, ALD;

- a thin carbon layer such as diamond, graphite carbon, deposited by ALD, PVD, CVD or inking of a sol-gel solution allowing to obtain after heat treatment a carbon-doped inorganic phase to make it conductive,
- a layer of conductive or semiconductor oxides, such as an ITO (indium-tin oxide) layer only deposited on the cathode substrate because the oxides are reduced at low potentials;
- a layer of conductive nitrides such as a TiN layer only deposited on the cathode substrate because nitrides insert lithium at low potentials.

The coating that can be used to protect the substrates serving as current collectors must be electronically conductive so as not to interfere with the operation of the electrode subsequently deposited on this coating, by making it too resistive.

In general, in order not to impact too heavily the operation of the battery cells, the maximum dissolution currents measured on the substrates which can act as a current collector, at the operating potentials of the electrodes, expressed in $\mu\text{A}/\text{cm}^2$, must be 1000 times lower than the surface capacities of the electrodes expressed in $\mu\text{Ah}/\text{cm}^2$. When seeking to increase the thickness of the electrodes, it is observed that the shrinkage generated by consolidation can lead either to cracking of the layers or to a shear stress at the interface between the substrate (which has a fixed dimension) and the ceramic electrode. When this shear stress exceeds a threshold, the layer detaches from its substrate.

To avoid this phenomenon, it is preferable to increase the thickness of the electrodes by a succession of deposition - sintering operations. This first variant of the first embodiment of the deposition of the layers gives a good result, but is not very productive. Alternatively, in a second variant, layers of greater thickness are deposited on both faces of a perforated substrate. The perforations must be of sufficient diameter so that the two layers of the front and back are in contact at the perforations. Thus, during consolidation, the nanoparticles and/or agglomerates of nanoparticles of electrode material in contact through the perforations in the substrate are welded together, forming an attachment point (welding point between the depositions of the two faces). This limits the loss of adhesion of the layers to the substrate during the consolidation steps.

To avoid this phenomenon, that is to say in order to increase the deposition thicknesses while limiting or eliminating the appearance of cracks, it is possible to add binders, dispersants. These additives and organic solvents can be eliminated by heat treatment, preferably under oxidising atmosphere, such as by debinding, during a sintering treatment or during a heat treatment carried out prior to the sintering treatment.

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3.2 Intermediate substrate

According to a second embodiment, the electrode layers are not deposited on a substrate capable of acting as an electric current collector, but on an intermediate, temporary substrate. In particular, it is possible to deposit, from suspensions that are more concentrated in nanoparticles and/or agglomerates of nanoparticles (that is to say less fluid, preferably pasty), fairly thick layers (called “green sheet”). These thick layers are deposited for example by a coating method, preferably by a doctor blade coating (a technique known under the term “tape casting”) or a slot-die coating. Said intermediate substrate may be a polymeric sheet, for example poly(ethylene terephthalate), abbreviated PET. During drying, these layers do not crack, in particular when drying occurs after the separation of the layer obtained in step (b) from its intermediate substrate. For consolidation by heat treatment (and preferably already for drying) they can be detached from their substrate; plates are thus obtained after cutting electrodes called “raw” electrodes which after calcination heat treatment and partial sintering will give mesoporous and self-supporting ceramic plates.

A stack of three layers is then made, namely two plates of electrodes of the same polarity separated by an electrically conductive sheet capable of acting as an electric current collector, such as a metal sheet or a graphite sheet. This stack is then assembled by a thermomechanical treatment, comprising a pressing and a heat treatment, preferably carried out simultaneously. Alternatively, to facilitate gluing between the ceramic plates and the metal sheet, the interface may be coated with a layer allowing electronically conductive gluing. This layer can be a sol-gel layer (preferably of the type allowing the chemical composition of the electrodes to be obtained after heat treatment) possibly loaded with particles of an electronically conductive material, which will make a ceramic weld between the mesoporous electrode and the metal sheet. This layer can also consist of a thin layer of non-sintered electrode nanoparticles, or of a thin layer of a conductive glue (loaded with graphite particles for example), or else a metallic layer of a metal having a low melting point. When said electrically conductive sheet is metallic, it is preferably a laminated sheet, that is to say obtained by lamination. The lamination may optionally be followed by a final annealing, which can be a (total or partial) softening or recrystallisation annealing, depending on the terminology of metallurgy. It is also possible to use an electrochemically deposited sheet, for example an electrodeposited copper sheet or an electrodeposited nickel sheet.

In any case, a ceramic electrode is obtained, without organic binder, which is mesoporous, located on either side of a metal substrate serving as an electronic current collector.

35 4. Deposition of the layers of active material P

In general, and as has already been mentioned, the electrodes according to the invention can be manufactured from suspensions of nanoparticles, using known coating techniques. These techniques which can be used are tape casting and coating techniques, such as roll coating, doctor blade coating, slot-die coating, curtain coating. Dip-coating can also be used.

For all these techniques, it is advantageous for the dry extract of the suspension to be greater than 20%, and preferably greater than 40%; this decreases the risk of cracking when drying.

Printing techniques can also be used, such as flexographic techniques, ink-jet printing.

Electrophoresis can also be used.

In a first embodiment, the method according to the invention advantageously uses the electrophoresis of suspensions of nanoparticles as a technique for depositing porous, preferably mesoporous, electrode layers. The method for depositing layers of electrodes from a suspension of nanoparticles is known as such (see for example EP 2 774 194 B1).

The substrate can be metallic, for example a metallic sheet. The substrate serving as a current collector within the batteries using porous electrodes according to the invention is preferably selected from strips of titanium, copper, stainless steel or molybdenum.

As a substrate, for example, a sheet of stainless steel with a thickness of 5 μm can be used. The metal sheet may be coated with a layer of noble metal, in particular selected from gold, platinum, palladium, titanium or alloys predominantly containing at least one or more of these metals, or with a layer of ITO type conductive material (which has the advantage of also acting as a diffusion barrier).

In a particular embodiment, a layer, preferably a thin layer, of an electrode material is deposited on the metal layer; this deposition must be very thin (typically a few tens of nanometres, and more generally comprised between 10 nm and 100 nm). It can be carried out by a sol-gel method. For example, LiMn_2O_4 can be used for a porous LiMn_2O_4 cathode. For electrophoresis to take place, a counter electrode is placed in the suspension and a voltage is applied between the conductive substrate and said counter electrode.

In an advantageous embodiment, the electrophoretic deposition of the aggregates or agglomerates of nanoparticles is carried out by galvanostatic electrodeposition in pulsed mode; high frequency current pulses are applied, this avoids the formation of bubbles on the surface of the electrodes and the variations of the electric field in the suspension during the deposition. The thickness of the electrode layer thus deposited by electrophoresis, preferably by galvanostatic electrodeposition in pulsed mode is advantageously less than 10 μm , preferably less than 8 μm , and is even more preferably between 1 μm and 6 μm .

To deposit layers that are quite thick by electrophoresis, carbon black nanoparticles can be added to the suspension to improve the electronic conduction of the deposition before consolidation. These carbon black nanoparticles will be removed by oxidation during the consolidation heat treatment.

5 In another embodiment, aggregates or agglomerates of nanoparticles can be deposited by the dip-coating method, regardless of the chemical nature of the nanoparticles used. This deposition method is preferred when the nanoparticles used have little or no electric charge. In order to obtain a layer of the desired thickness, the step of depositing by dip-coating the aggregates or agglomerates of nanoparticles followed by the step of drying the resulting
10 layer are repeated as necessary. In order to increase the thickness of the layers free of cracks, it is advantageous to use in the colloidal suspension or the deposited paste, at least one organic additive such as ligands, stabilisers, thickeners, binders or residual organic solvents. Although this succession of dip-coating/drying steps is time consuming, the dip-coating deposition method is a method which is simple, safe, easy to implement, to
15 industrialise and allowing to obtain a homogeneous and compact final layer.

5. Consolidation treatment of the deposited layers

The deposited layers must be dried; drying must not induce the formation of cracks. For this reason, it is preferred to carry it out under controlled humidity and temperature conditions
20 or to use, to produce the porous layer, colloidal suspensions and/or pastes comprising, in addition to aggregates or agglomerates of monodisperse primary nanoparticles, at least one electrode active material P according to the invention, organic additives such as ligands, stabilisers, thickeners, binders or residual organic solvents.

The dried layers can be consolidated by a pressing and/or heating step (heat treatment). In
25 a very advantageous embodiment of the invention, this treatment leads to a partial coalescence of the primary nanoparticles in the aggregates, or agglomerates, and between neighbouring aggregates or agglomerates; this phenomenon is called "necking" or "neck formation". It is characterised by the partial coalescence of two particles in contact, which remain separate but connected by a (constricted) neck; this is illustrated schematically in
30 Figures 3 and 4. Lithium ions and electrons are movable within these necks and can diffuse from particle to particle without encountering grain boundaries. The nanoparticles (Figure 3) are welded together to ensure the conduction of electrons from one particle to another (Figure 4). Thus, a continuous mesoporous film forming a three-dimensional network with high ionic mobility and electronic conduction, is formed from the primary nanoparticles; this
35 network includes interconnected pores, preferably mesopores.

The temperature necessary to obtain “necking” depends on the material; taking into account the diffusive nature of the phenomenon which leads to necking, the duration of the treatment depends on the temperature. This method can be called sintering; depending on its duration and temperature, a more or less pronounced coalescence (necking) is obtained, which has
 5 repercussions on the porosity. It is thus possible to go down to 30% (or even 25%) of porosity while maintaining a perfectly homogeneous channel size.

The heat treatment can also be used to eliminate the organic additives possibly contained in the suspension of nanoparticles used, such as ligands, stabilisers, binders or residual organic solvents. According to another variant, an additional heat treatment, under an
 10 oxidising atmosphere, can be carried out to remove these organic additives possibly contained in the suspension of nanoparticles used. This additional heat treatment is advantageously carried out on the porous layer separated from its intermediate substrate, when such a substrate is used. This additional heat treatment is advantageously carried out before the consolidation treatment of step c) allowing to obtain a porous, preferably
 15 mesoporous, layer.

6. Deposition of the coating of electronically conductive material

According to an essential feature of the present invention, a coating of an electronically conductive material is deposited on and inside the pores of said porous layer.
 20 Indeed, as explained above, the method according to the invention, which necessarily involves a step of depositing agglomerated nanoparticles of electrode material (active material), causes the nanoparticles to “weld” naturally to each other to generate, after consolidation such as annealing, a porous, rigid, three-dimensional structure, without organic binder; this porous, preferably mesoporous, layer, is perfectly adapted to the
 25 application of a surface treatment, by gas or liquid, which goes deep into the open porous structure of the layer.

Very advantageously, this deposition is carried out by a technique allowing an encapsulating coating (also called “conformal deposition”), a deposition which faithfully reproduces the atomic topography of the substrate on which it is applied, and which goes
 30 deep into the open porosity network of the layer. Said electronically conductive material may be carbon.

The techniques of ALD (Atomic Layer Deposition) or CSD (Chemical Solution Deposition), known as such, may be suitable. They can be implemented on the porous layers after manufacture, before the deposition of the separator particles and before the assembly of
 35 the cell. The ALD deposition technique is carried out layer by layer, by a cyclic method, and allows to produce an encapsulating coating which faithfully reproduces the topography of

the substrate; the coating lines the entire surface of the electrodes. This encapsulating coating typically has a thickness comprised between 1 nm and 5 nm.

The deposition by ALD is carried out at a temperature typically comprised between 100°C and 300°C. It is important that the layers are free from organic matter: they must not include
 5 any organic binder, any residues of stabilising ligands used to stabilise the suspension must have been removed by purification of the suspension and/or during the heat treatment of the layer after drying. Indeed, at the temperature of the ALD deposition, the organic materials forming the organic binder (for example the polymers contained in the electrodes produced by ink tape casting) risk decomposing and will pollute the ALD reactor. Moreover,
 10 the presence of residual polymers in contact with the electrode active material particles can prevent the ALD coating from encapsulating all the particle surfaces, which impairs its effectiveness.

The CSD deposition technique also allows to produce an encapsulating coating with a precursor of the electronically conductive material which faithfully reproduces the
 15 topography of the substrate; it lines the entire surface of the electrodes. This encapsulating coating typically has a thickness of less than 5 nm, preferably comprised between 1 nm and 5 nm. It must then be transformed into an electronically conductive material. In the case of a carbon precursor, this will be done by pyrolysis, preferably under inert gas (such as nitrogen).

20 In this variant of depositing a nanolayer of electronically conductive material, it is preferable that the diameter D_{50} of the primary particles of electrode material is at least 10 nm in order to prevent the conductive layer from blocking the open porosity of the electrode layer.

7. Electrolyte

25 The electrolyte is not part of the present invention, but it is useful to mention it here because it is needed to form the battery cell. The electrode according to the invention does not contain organic compounds. This absence of organic compounds coupled to a mesoporous structure promotes wetting by an electrolyte which conducts lithium ions. This electrolyte can then be selected without distinction from the group formed of: an electrolyte composed
 30 of aprotic solvents and lithium salts, an electrolyte composed of ionic liquids or poly(ionic liquids) and lithium salts, a mixture of aprotic solvents and ionic liquids or poly(ionic liquids) and lithium salts, a polymer made ionically conductive containing lithium salts, an ionically conductive polymer.

Said ionic liquids can be salts molten at room temperature (these products are known under
 35 the designation RTIL, Room Temperature Ionic Liquid), or ionic liquids which are solid at room temperature. These ionic liquids which are solid at room temperature must be heated

in order to liquefy them in order to impregnate the electrodes; they are solidified in the electrode. Said ionically conductive polymer can be melted to be mixed with the lithium salt and this molten phase can then be impregnated into the mesoporosity of the electrode.

Likewise, said polymer can be a liquid at room temperature, or else a solid, which is then
 5 heated to make it liquid in order to impregnate it in the mesoporous electrode.

8. Examples of advantageous embodiments

In general, when the lithium-ion battery has to operate at high temperature, use is advantageously made, as the material P for the cathode, of one of the materials listed above
 10 from those which does not contain manganese, such as LiFePO_4 or LiCoPO_4 . The anode in this case is advantageously a titanate, a mixed oxide of titanium and niobium or a derivative of a mixed oxide of titanium and niobium, and the cell is impregnated with an ionic liquid including a lithium salt. If said ionic liquid includes sulphur atoms, it is preferred that the substrate is a noble metal.

15 To enable the person skilled in the art to carry out the method according to the invention, some embodiments and examples of electrodes according to the invention are given here. In a first advantageous embodiment, a mesoporous anode is manufactured according to the invention for a lithium-ion battery with a suspension of material P which is $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or $\text{Li}_4\text{Ti}_{5-x}\text{M}_x\text{O}_{12}$ with $\text{M} = \text{V}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta}$. Figure 1 shows a typical X-ray diffractogram of the
 20 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanopowder used in the suspension, Figure 2 shows a picture obtained by transmission electron microscopy of these primary nanoparticles.

This material is deposited on a metal substrate, which is heat treated (sintered) and covered with a layer of an electronically conductive material a few nanometres thick; this layer is called here "nanocoating". This nanocoating is preferably carbon. This carbon nanocoating
 25 can be produced by impregnation with a carbon-rich liquid phase, which is then pyrolysed under nitrogen, or else by ALD deposition. These anodes insert lithium at a potential of 1.55 V, are very powerful and allow ultra-fast recharging.

In a second advantageous embodiment, a mesoporous anode according to the invention is manufactured for a lithium-ion battery with a material P which is TiNb_2O_7 or $\text{Li}_w\text{Ti}_{1-x}\text{M}^1_x\text{Nb}_{2-y}\text{M}^2_y\text{O}_7$, wherein M^1 and M^2 are each at least one element selected from the group consisting
 30 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^1 and M^2 can be identical or different from each other, and wherein $0 \leq w \leq 5$, $0 \leq x \leq 1$, $0 \leq y \leq 2$. This layer is deposited on a metal substrate, sintered and covered with an electronically conductive nanocoating, which is advantageously carbon, deposited as
 35 described in relation to the previous embodiment. These anodes are very powerful and allow rapid recharging.

In a third advantageous embodiment, a mesoporous anode is manufactured according to the invention for a lithium-ion battery with a material P which is $\text{Nb}_2\text{O}_{5\pm\delta}$ or $\text{Nb}_{18}\text{W}_{16}\text{O}_{93\pm\delta}$ or $\text{Nb}_{16}\text{W}_5\text{O}_{55\pm\delta}$ with $0 \leq x < 1$ and $0 \leq \delta \leq 2$, or $\text{La}_x\text{Ti}_{1-2x}\text{Nb}_{2+x}\text{O}_7$ where $0 < x < 0.5$; or $\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$ or $\text{Li}_w\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$ or $\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$ or $\text{Li}_w\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$ wherein

5 M^1 is at least one element selected from 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 and where $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$; or $\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$ or $\text{Li}_w\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$ or $\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$ or $\text{Li}_w\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$ wherein M^1 and M^2 are

10 Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs, Ce and Sn, M^1 and M^2 may be identical or different from each other, and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$. This layer is deposited on a metallic substrate, sintered and covered with an electronically conductive nanocoating, which is advantageously carbon, deposited as described in relation to the previous embodiment. These anodes are very powerful and

15 allow rapid recharging.

In a fourth embodiment, a mesoporous anode is manufactured according to the invention for a lithium-ion battery with a material P which is $\text{TiNb}_2\text{O}_{7-z}\text{M}^3_z$ or $\text{Li}_w\text{Ti}_{1-x}\text{M}^1_x\text{Nb}_{2-y}\text{M}^2_y\text{O}_{7-z}\text{M}^3_z$ wherein M^1 and M^2 are each at least one element selected from the group consisting of Nb,

20 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^1 and M^2 can be identical or different from each other. The relationship $0 \leq w \leq 5$, $0 \leq x \leq 1$, and $0 \leq y \leq 2$ is applied. M^3 is at least one halogen and $z \leq 0.3$. As described in relation to the second embodiment, this layer is deposited on a metal substrate, sintered and covered with a nanocoating, which may be carbon, deposited as described above.

25 These anodes are very powerful and are capable of rapid recharges.

In a fifth embodiment, a mesoporous anode is manufactured according to the invention for a lithium-ion battery with a material P which is TiO_2 or LiSiTON ; the manufacture is carried out as described in relation to the other embodiments. These electrodes are very powerful and are capable of rapid recharges.

30 In a sixth exemplary embodiment, a mesoporous cathode is manufactured according to the invention for a lithium-ion battery with a material P which is LiMn_2O_4 ; these nanoparticles can be obtained by hydrothermal synthesis using the procedures described in the article "One pot hydrothermal synthesis and electrochemical characterisation of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinel structured compounds", published in the journal Energy Environ. Sci., 3, p. 1339-1346. In

35 this synthesis, a small amount of PVP was added in order to adjust the size and shape of the agglomerates obtained. The latter are spherical in shape and approximately 150 nm in

diameter, consisting of primary particles comprised between 10 nm and 20 nm in size. After centrifugation and washing, about 10 to 15% by mass of PVP 360k were added to the aqueous suspension and the water was evaporated to obtain a dry extract of 10%. The ink thus obtained was applied to a sheet of stainless steel and then dried to obtain a layer of approximately 10 microns. This sequence can be repeated several times to increase the thickness of the deposition. The deposition thus obtained was annealed for 1 hour at 600°C under air in order to consolidate the agglomerates of nanoparticles to each other.

This mesoporous layer was then impregnated with a sucrose solution, then annealed at 400°C under nitrogen to obtain an electronically conductive carbon layer over the entire mesoporous surface of the electrode; the thickness of this carbon layer was of a few nanometres. The electrolyte layer, in this case Li_3PO_4 , which will subsequently be impregnated, was then deposited on this mesoporous cathode. In a sixth exemplary embodiment, a battery is manufactured according to the invention, said battery is formed of:

- A mesoporous anode (50% porosity) comprising $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and/or TiO_2 ,
- A mesoporous cathode (50% porosity) comprising LiMn_2O_4 ,
- A mesoporous electrolytic separator (50% porosity) comprising Li_3PO_4 .

The electrode substrates were made of 316L stainless steel. The ionic impregnation liquid was a mixture of 1-butyl-1-methylpyrrolidinium bis(trifluoromethane sulfonyl)imide (abbreviated Pyr14TFSI) and lithium bis(fluorosulfonyl)imide (abbreviated LiTFSI) at 0.7 M. Figure 5 shows the evolution of the relative capacity of a battery according to the invention depending on the number of charge and discharge cycles; each discharge was carried out to a depth of 100% of the battery capacity. It is observed that there is no loss of the relative capacity of the battery; the battery according to the invention has an excellent durability in terms of charge-discharge cycles.

Figure 6 shows a recharging curve of this battery. It is seen that 80% of the battery capacity can be recharged in just less than 5 minutes; this rapid recharging capacity is of enormous application benefit.

CLAIMS

1. A method for manufacturing a porous electrode, in particular for electrochemical devices, said electrode comprising a porous layer deposited on a substrate, said layer being free of binder, having a porosity comprised between 20% and 60% by volume, preferably
5 between 25% and 50%, and pores with an average diameter of less than 50 nm, said manufacturing method being characterised in that:
 - (a) provision is made of a substrate and a colloidal suspension or a paste comprising aggregates or agglomerates of monodisperse primary nanoparticles, of at least one active electrode material P, having an average primary diameter D_{50} comprised
10 between 2 nm and 150 nm, preferably between 2 nm and 100 nm, and more preferably between 2 nm and 60 nm, said aggregates or agglomerates having an average diameter D_{50} comprised between 50 nm and 300 nm, and preferably between 100 nm to 200 nm,
 - (b) a layer is deposited from said colloidal suspension or paste provided in step (a) on
15 at least one face of said substrate by a method selected from the group formed of: electrophoresis, a printing method and preferably ink-jet printing or flexographic printing, a coating method and preferably doctor blade coating, roll coating, curtain coating, dip-coating, or slot-die coating;
 - (c) said layer obtained in step (b) is dried, where appropriate, before or after having
20 separated said layer from its intermediate substrate, then, optionally, said dried layer is heat treated, preferably under an oxidising atmosphere, and it is consolidated, by pressing and/or heating, to obtain a porous, preferably mesoporous, layer,
 - (d) depositing, on and inside the pores of said porous layer, a coating of an electronically conductive material,
- 25 knowing that said substrate may be a substrate capable of acting as an electric current collector, or an intermediate substrate.
2. The method according to claim 1, characterised in that said porous layer resulting from step (c) has a specific surface comprised between 10 m²/g and 500 m²/g.
3. The method according to any one of claims 1 to 2, wherein said porous layer
30 obtained in step (c) has a thickness comprised between 4 µm and 400 µm.
4. The method according to any one of claims 1 to 3, characterised in that when said substrate is an intermediate substrate, said layer is separated in step (c) before or after the drying of said intermediate substrate, to form a porous plate.
5. The method, characterised in that when said colloidal suspension or paste provided
35 in step (a) comprises organic additives, such as ligands, stabilisers, binders or residual organic solvents, said layer dried in step c) is heat treated, preferably under an oxidising

- atmosphere, according to any one of claims 1 to 3, or said porous plate according to claim 4.
6. The method according to any one of claims 1 to 5, characterised in that said electronically conductive material is carbon.
- 5 7. The method according to any one of claims 1 to 6, characterised in that the deposition of said coating of electronically conductive material is carried out by the atomic layer deposition ALD technique or by immersion of the porous layer in a liquid phase including a precursor of said electronically conductive material, followed by the transformation of said precursor into electronically conductive material.
- 10 8. The method according to claim 7, characterised in that said precursor is a carbon-rich compound, such as a carbohydrate, preferably a polysaccharide, and in that said transformation into an electronically conductive material is a pyrolysis, preferably under an inert atmosphere.
9. The method according to any one of claims 1 to 8, wherein said material P is
15 selected from the group formed of:
- o the oxides LiMn_2O_4 , $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ with $0 < x < 0.15$, 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 $0 < x < 0.1$, $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ with $\text{M} = \text{Er, Dy, Gd, Tb, Yb, Al, Y, Ni, Co, Ti, Sn, As, Mg}$ or
20 a mixture of these compounds and where $0 < x < 0.4$, LiFeO_2 , $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ with $0 \leq x < 0.15$, $\text{LiNi}_{1/x}\text{Co}_{1/y}\text{Mn}_{1/z}\text{O}_2$ with $x+y+z=10$;
 - o $\text{Li}_x\text{M}_y\text{O}_2$ where $0.6 \leq y \leq 0.85$; $0 \leq x+y \leq 2$; and M is selected from Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Sn, and Sb or a mixture of these elements; $\text{Li}_{1.20}\text{Nb}_{0.20}\text{Mn}_{0.60}\text{O}_2$;
 - 25 o $\text{Li}_{1+x}\text{Nb}_y\text{Me}_z\text{A}_p\text{O}_2$ where Me is at least one transition metal selected from: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Rf, Db, Sg, Bh, Hs and Mt, and where $0.6 < x < 1$; $0 < y < 0.5$; $0.25 \leq z < 1$; with $\text{A} \neq \text{Me}$ and $\text{A} \neq \text{Nb}$, and $0 \leq p \leq 0.2$;
 - o $\text{Li}_x\text{Nb}_{y-a}\text{NaM}_{z-b}\text{P}_b\text{O}_{2-c}\text{F}_c$ where $1.2 < x \leq 1.75$; $0 \leq y < 0.55$; $0.1 < z < 1$; $0 \leq a < 0.5$; $0 \leq b < 1$;
30 $0 \leq c < 0.8$; and where M, N, and P are each at least one of the elements selected from the group consisting of Ti, Ta, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Zr, Y, Mo, Ru, Rh, and Sb;
 - o $\text{Li}_{1.25}\text{Nb}_{0.25}\text{Mn}_{0.50}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.40}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Fe}_{0.40}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.43}\text{Ni}_{0.27}\text{O}_2$;
 $\text{Li}_{1.3}\text{Nb}_{0.43}\text{Co}_{0.27}\text{O}_2$; $\text{Li}_{1.4}\text{Nb}_{0.2}\text{Mn}_{0.53}\text{O}_2$;
 - 35 o $\text{Li}_x\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_y$ where $0.00 \leq x \leq 1.52$; $1.07 \leq y < 2.4$; $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$;

- o $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ where $0 \leq x$ and $y \leq 0.5$; $\text{LiNi}_x\text{Ce}_z\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ where $0 \leq x$ and $y \leq 0.5$ and $0 \leq z$;
 - o phosphates LiFePO_4 , LiMnPO_4 , LiCoPO_4 , LiNiPO_4 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, $\text{Li}_2\text{MPO}_4\text{F}$ with $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ or a mixture of these different elements, LiMPO_4F with $\text{M} = \text{V}, \text{Fe}, \text{T}$ or a mixture of these different elements; the phosphates of formula $\text{LiMM}'\text{PO}_4$, with M and M' ($\text{M} \neq \text{M}'$) selected from $\text{Fe}, \text{Mn}, \text{Ni}, \text{Co}, \text{V}$ such as the $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ and where $0 < x < 1$;
 - o $\text{Fe}_{0.9}\text{Co}_{0.1}\text{OF}$; LiMSO_4F with $\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}, \text{Mg}$;
 - o all lithiated forms of the following chalcogenides: V_2O_5 , V_3O_8 , TiS_2 , titanium oxysulfides (TiO_yS_z with $z=2-y$ and $0.3 \leq y \leq 1$), tungsten oxysulfides (WO_yS_z with $0.6 < y < 3$ and $0.1 < z < 2$), CuS , CuS_2 , preferably $\text{Li}_x\text{V}_2\text{O}_5$ with $0 < x \leq 2$, $\text{Li}_x\text{V}_3\text{O}_8$ with $0 < x \leq 1.7$, Li_xTiS_2 with $0 < x \leq 1$, titanium and lithium oxysulfides with $\text{Li}_x\text{TiO}_y\text{S}_z$ with $z=2-y$, $0.3 \leq y \leq 1$ and $0 < x \leq 1$, $\text{Li}_x\text{WO}_y\text{S}_z$ with $z=2-y$, $0.3 \leq y \leq 1$ and $0 < x \leq 1$, Li_xCuS with $0 < x \leq 1$, Li_xCuS_2 with $0 < x \leq 1$.
10. The method according to any one of claims 1 to 8, wherein said material P is selected from the group formed of:
- o $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_4\text{Ti}_{5-x}\text{M}_x\text{O}_{12}$ with $\text{M} = \text{V}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta}$ and $0 \leq x \leq 0.25$;
 - o niobium oxides and mixed niobium oxides with titanium, germanium, cerium or tungsten, and preferably from the group formed of:
 - o $\text{Nb}_2\text{O}_{5 \pm \delta}$, $\text{Nb}_{18}\text{W}_{16}\text{O}_{93 \pm \delta}$, $\text{Nb}_{16}\text{W}_5\text{O}_{55 \pm \delta}$ with $0 \leq x < 1$ and $0 \leq \delta \leq 2$, LiNbO_3 ,
 - o $\text{TiNb}_2\text{O}_{7 \pm \delta}$, $\text{Li}_w\text{TiNb}_2\text{O}_7$ with $w \geq 0$, $\text{Ti}_{1-x}\text{M}^1_x\text{Nb}_{2-y}\text{M}^2_y\text{O}_{7 \pm \delta}$ or $\text{Li}_w\text{Ti}_{1-x}\text{M}^1_x\text{Nb}_{2-y}\text{M}^2_y\text{O}_{7 \pm \delta}$ wherein M^1 and M^2 are each at least one element selected from the group consisting of $\text{Nb}, \text{V}, \text{Ta}, \text{Fe}, \text{Co}, \text{Ti}, \text{Bi}, \text{Sb}, \text{As}, \text{P}, \text{Cr}, \text{Mo}, \text{W}, \text{B}, \text{Na}, \text{Mg}, \text{Ca}, \text{Ba}, \text{Pb}, \text{Al}, \text{Zr}, \text{Si}, \text{Sr}, \text{K}, \text{Cs}$ and Sn , M^1 and M^2 can be identical or different from each other, and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $0 \leq \delta \leq 0.3$;
 - o $\text{La}_x\text{Ti}_{1-2x}\text{Nb}_{2+x}\text{O}_7$ where $0 < x < 0.5$;
 - o $\text{M}_x\text{Ti}_{1-2x}\text{Nb}_{2+x}\text{O}_{7 \pm \delta}$
 - o wherein M is an element whose degree of oxidation is +III, more particularly M is at least one of the elements selected from the group consisting of $\text{Fe}, \text{Ga}, \text{Mo}, \text{Al}, \text{B}$, and where $0 < x \leq 0.20$ and $-0.3 \leq \delta \leq 0.3$;
 $\text{Ga}_{0.10}\text{Ti}_{0.80}\text{Nb}_{2.10}\text{O}_7$; $\text{Fe}_{0.10}\text{Ti}_{0.80}\text{Nb}_{2.10}\text{O}_7$;
 - o $\text{M}_x\text{Ti}_{2-2x}\text{Nb}_{10+x}\text{O}_{29 \pm \delta}$
 - o wherein M is an element whose degree of oxidation is +III, more particularly M is at least one of the elements selected from the group consisting of $\text{Fe}, \text{Ga}, \text{Mo}, \text{Al}, \text{B}$, and where $0 < x \leq 0.40$ and $-0.3 \leq \delta \leq 0.3$;
 - o $\text{Ti}_{1-x}\text{M}^1_x\text{Nb}_{2-y}\text{M}^2_y\text{O}_{7-z}\text{M}^3_z$ or $\text{Li}_w\text{Ti}_{1-x}\text{M}^1_x\text{Nb}_{2-y}\text{M}^2_y\text{O}_{7-z}\text{M}^3_z$ wherein

- o M^1 and M^2 are each at least one element selected from 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,
 - o M^1 and M^2 can be identical or different from each other,
 - 5 o M^3 is at least one halogen,
 - o and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
 - o $TiNb_2O_{7-z}M^3_z$ or $Li_wTiNb_2O_{7-z}M^3_z$ wherein M^3 is at least one halogen, preferably selected from F, Cl, Br, I or a mixture thereof, and $0 < z \leq 0.3$;
 - 10 o $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7\pm z}$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7\pm z}$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7\pm z}$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7\pm z}$ wherein
 - o M^1 is at least one element selected from 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;
 - o $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
 - 15 o $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$, wherein
 - o M^1 and M^2 are each at least one element selected from 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, Ce and Sn,
 - 20 o M^1 and M^2 can be identical or different from each other,
 - o and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
 - o TiO_2 ;
 - o LiSiTON.
11. A porous electrode having a porosity comprised between 20% and 60% by volume,
- 25 free of binder, comprising pores with an average diameter of less than 50 nm, that can be obtained by the method according to any one of claims 1 to 10.
12. A use of a method according to any one of claims 1 to 10 for manufacturing porous electrodes in lithium-ion batteries.
13. A method for manufacturing a battery designed to have a capacity not exceeding 1
- 30 mAh, implementing the method for manufacturing a porous electrode according to one of claims 1 to 10, or implementing a porous electrode according to claim 11.
14. The method according to claim 13, characterised in that said battery is a lithium-ion battery.
15. The method according to claim 13 or 14, wherein the method for manufacturing a
- 35 porous electrode according to claim 11 is implemented to manufacture a cathode or the method according to claim 11 is implemented to manufacture an anode.

16. The method according to any one of claims 13 to 15, wherein said porous electrode is impregnated with an electrolyte, preferably a phase carrying lithium ions selected from the group formed of:
- o an electrolyte composed of at least one aprotic solvent and at least one lithium salt;
 - 5 o an electrolyte composed of at least one ionic liquid and at least one lithium salt;
 - o a mixture of at least one aprotic solvent and at least one ionic liquid and at least one lithium salt;
 - o a polymer made ionically conductive by adding at least one lithium salt; and
 - o a polymer made ionically conductive by adding a liquid electrolyte, either in the
 - 10 polymer phase or in the mesoporous structure.
17. A lithium-ion battery designed to have a capacity not exceeding 1 mAh, that can be obtained by the method according to any one of claims 13 to 16.