

DESCRIPTION

Title: **PROCESS FOR MANUFACTURING A POROUS ELECTRODE, AND BATTERY CONTAINING SUCH AN ELECTRODE**

5 **Field of the invention**

The invention relates to energy storage or production devices. More precisely, it relates to electrodes that can be used in energy storage or production devices such as capacitors, photovoltaic cells or ion insertion batteries, in particular lithium-ion batteries, sodium-ion batteries and potassium-ion batteries. The invention applies to negative electrodes and to
10 positive electrodes. It relates to porous electrodes which can be impregnated by an ionic conducting phase such as a solid electrolyte without liquid phase or a liquid electrolyte.

The invention also relates to a method for preparing such a porous electrode which uses aggregates or agglomerates of nanoparticles of an electrode material and at least one oxide electronic conductor material precursor, and the electrodes thus obtained. The invention
15 also relates to a method for producing an energy storage or production device, in particular to a method for producing a lithium-ion battery comprising at least one of these electrodes, and the batteries thus obtained.

Prior art

20 Among the various commercially-available electrochemical storage technologies, lithium-ion batteries have the best energy density. There are various architectures and chemical compositions of electrodes that can be used to produce these batteries. The methods for producing lithium-ion batteries are presented in many articles and patents; a review is given in the publication "*Advances in lithium-Ion Batteries*" (ed. W. van Schalkwijk and B.
25 Scrosati), published in 2002 (Kluwer Academic/Plenum Publishers).

There is a growing need for very small size rechargeable batteries, which can be incorporated onto electronic boards; these electronic circuits can be used in many fields, for example in cards for securing transactions, in electronic tags, in implantable medical devices and in various micro-mechanical systems.

30 There is also a growing need for high-capacity rechargeable batteries, in particular for supplying transport devices (electric bicycles, scooters, electric motorbikes, electric cars, electric commercial vehicles) and for the storage of electrical energy, for example for storing electricity produced by intermittent electricity generators (wind turbines, photovoltaic panels) or for stabilising an electrical grid that is subject to highly fluctuating supply and
35 demand.

There is also a growing need for intermediate size rechargeable batteries for various autonomous and portable devices (for example mobile telephones, portable computers, portable power tools, intermittent usage kitchen appliances).

15 In all these applications, the possibility of rapid recharging of the battery is a highly desirable feature. Similarly, these batteries must not present a risk of thermal runaway. Finally, it is desirable that they can operate within a large temperature range.

10 According to the prior art, electrodes for lithium-ion batteries can be produced by covering techniques, in particular by coating. These methods make it possible to deposit, on the surface of a substrate, an ink consisting of particles of active materials in powder form; the particles constituting this powder having a average particle size which is typically between 5 μm and 15 μm diameter.

15 These deposition techniques, in particular by coating, make it possible to produce layers with a thickness of between approximately 20 μm and approximately 400 μm . The power and energy of the battery can be modulated by adjusting the thickness and porosity of the layers, the size of the active particles which constitute it and through the presence of various constituents within the layer, such as binders or electronic conductor materials. In order to produce microbatteries, it is desirable to have a lower thickness of each layer constituting the microbattery.

20 In addition to the problems related to the formulation of inks in order to obtain a high-performance electrode with low production cost, it must be kept in mind that the ratio between the energy density and the power density of the electrodes can be adjusted as a function of the size of the particles of active materials, and indirectly by the specific surface area of the electrode layers and their thickness. 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 thickness of the electrodes and their porosity on their discharging regime (power) and energy density.

30 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 with a liquid electrolyte, but their electrical resistivity remains rather high.

In order to increase the low electronic conductivity of electrodes, especially when these electrodes are of high thickness or produced from electrode active materials with low electronic conductivity, a certain quantity of electronic conductor material, such as carbon black, is generally added to the particles of electrode active material. Ideally, the particles of electronic conductor should be available at any point on the surface of the particle of

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electrode active material in order to enable a simultaneous insertion/extraction over the entire surface of the electrode active particles, thus maximising the current density and minimising the stress and local heating due to inhomogeneous electrical transport.

In practice, it is very difficult to control the disposition of carbon black within the electrodes.

5 Moreover, with the increasing use of smaller and smaller particles of active material, these problems are ever more pervasive. A non-uniform distribution of carbon black in the electrode induces a much higher polarisation of the electrode, which leads to an increase in the series resistance of the battery comprising such an electrode. These imbalances in local charge state will be all the more pronounced the higher the current density. These
10 imbalances consequently induce a loss in cycle performance, a safety risk and a power limitation of the battery cell. The same applies when the electrodes have an inhomogeneous porosity, i.e. distributed in size; this inhomogeneity contributes to making the wetting of the electrode pores more difficult

In this context and in order to reduce the electrical resistivity of the electrodes, the applicant
15 has developed a mesoporous electrode comprising a mesoporous layer of at least one electrode active material having a carbon coating on and inside the pores of this mesoporous layer; this is known from WO 2021/220 174 (I-TEN). The presence of this carbon electronic conductor coating on the electrode can reduce its electrical resistivity but does not significantly increase its voltage, temperature and electrochemical stability.
20 Moreover, the production of a carbon electronic conductor coating on the electrode is expensive and difficult to implement.

As there is a growing need for very small size rechargeable batteries, the electrodes must meet increasingly stringent specifications. They must have a high chemical and electrochemical stability, solidity and corrosion resistance, so as to give the batteries
25 comprising them high cycle performances, storage stability, temperature stability, and long-term reliability and combine high energy density with high power density. The present invention seeks to overcome at least some of the disadvantages of the prior art mentioned above.

More precisely, the problem that the present invention seeks to solve is that of providing a
30 method for producing porous electrodes having a high, homogeneous electronic conductivity and a controlled pore density which is simple, safe, quick and easy to implement and inexpensive.

The present invention also aims to provide safe porous electrodes having a high electronic conductivity, stable mechanical structure, good thermal stability, in particular at high
35 temperature and a long service life, and to do so whatever the thickness of the electrode,

Another aim of the invention is to provide electrodes for batteries capable of operating at high temperature without problems of reliability and without the risk of fire.

Another aim of the invention is to provide porous electrodes which, in addition to the preceding features, can be easily wetted and impregnated by an ionic liquid or a polymer.

5 Another aim of the invention is to provide a method for producing an energy storage or production device such as a capacitor, supercapacitor, hybrid supercapacitor, photovoltaic cell, photochemical cell or battery, in particular a lithium-ion battery, sodium-ion battery or even a potassium-ion battery, comprising a porous electrode according to the invention.

Yet another aim of the invention is to provide energy storage or production devices such as
10 batteries, in particular lithium-ion batteries and microbatteries, capacitors, supercapacitors, hybrid supercapacitors, such as lithium-ion hybrid supercapacitors, hereinafter LiC, sodium-ion hybrid supercapacitors, hereinafter SIHC, potassium-ion hybrid supercapacitors, hereinafter PIHC, capable of storing high energy densities, restoring this energy with very high power densities (in particular in capacitors or supercapacitors), withstanding high
15 temperatures, having an excellent cycling service life, as well as increased safety.

Objects of the invention

In order to increase the performance of electrodes which can be used in energy storage or
20 production devices, in particular in conventional lithium-ion batteries, in particular by reducing their electrical resistivity while significantly increasing their voltage, temperature and electrochemical stability, the inventors have sought an alternative to the carbon electronic conductor coating presented in application WO 2021/220 174 (I-TEN).

According to the invention, the problem is solved by an electrode for lithium-ion, sodium-ion
25 or potassium-ion batteries, which is totally ceramic, porous, free of organic binders and the porosity of which is between 25% and 60% by volume. The electrode according to the invention is a porous, preferably mesoporous, layer comprising at least one electrode active material and an oxide electronic conductor material, the porosity of which is between 25% and 60% by volume. Advantageously, the electrode according to the invention comprises
30 zones of electrode active material P, at least partially covered by a coating of an oxide electronic conductor material throughout the internal volume of the electrode as well as at the surface, preferably the electrode according to the invention comprises zones of electrode active material P covered with a coating of an oxide electronic conductor material throughout the internal volume of the electrode as well as on the surface.

35 This entirely solid, porous, preferably mesoporous, layer, without organic components, is obtained from agglomerates and/or aggregates of primary nanoparticles of at least one

electrode active material and of at least one oxide electronic conductor material precursor. The sizes of the primary particles constituting these agglomerates and/or aggregates are of order nanometres or tens of nanometres, and the agglomerates and/or aggregates contain at least four primary particles.

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

The fact of using agglomerates of several tens or even several hundreds of nanometres in diameter, rather than non-agglomerated primary particles, each with a size on the order of
 10 a nanometre or ten nanometres, enables the thickness of the deposit to be increased. However, the agglomerates must remain small in order to be able to form, during the heat treatment of the layer, a continuous mesoporous film. If the agglomerates are too large, this will harm their sintering and the formation of two distinct porosities will be seen in the layer: a porosity between agglomerates and a porosity inside the agglomerates.

- 15 After sintering, a porous, preferably mesoporous, layer or a plate, without carbon black or organic binders is obtained, in which all the primary nanoparticles are welded together (by the phenomenon of necking, known elsewhere) in order to form a continuous mesoporous network, characterised by a unimodal porosity. The porous, preferably mesoporous, layer thus obtained is entirely solid and ceramic. There is no longer a risk of loss of electrical
 20 contact between the particles of active materials during cycling, which improves the cycle performance of the battery. Furthermore, after sintering, the porous, preferably mesoporous, layer adheres perfectly on the metal substrate on which it is deposited or transferred (in the case of an initial deposition made on an intermediate substrate).

The thermal treatment is carried out at high temperature in order to sinter together the
 25 nanoparticles, making it possible to perfectly dry the electrode and remove any traces of water or solvents or other organic additives (stabilisers, binders) absorbed at the surface of the particles of active material. The high-temperature heat treatment (sintering) can be preceded by a lower-temperature heat treatment (debinding) in order to dry the placed or deposited electrode and to remove the traces of water or solvents or other organic additives
 30 (stabilisers, binders) absorbed at the surface of the particles of active material; this debinding can be performed in an oxidising atmosphere.

It is possible to adjust the porosity of the final electrode as a function of the sintering time and temperature. The porosity can be adjusted in a range between 25% and 60% depending on the energy density needs.

- 35 In any event, the power density of the electrodes thus obtained remains extremely high due to the porosity, preferably due to the mesoporosity. Furthermore, independently of the size

of the mesopores in the active material (understanding that after sintering the notion of a nanoparticle no longer applies to the material which now has a three-dimensional structure with a network of channels and mesopores), the dynamic equilibrium of the cell remains perfect, which contributes to maximising the power density and service life of the battery cell.

5 The electrode according to the invention has a high specific surface area, which reduces the ionic resistance of the electrode. However, in order that this electrode delivers a maximum of power, it still needs to have a very good electronic conductivity in order to avoid ohmic losses in the battery. This improvement in the electronic conductivity of the cell will
10 be all the more critical the larger the thickness of the electrode. Furthermore, this electronic conductivity must be perfectly homogeneous throughout the electrode in order to avoid having local zones which are more electrically resistive, which could lead to the formation of a hotspot during the power operation of the battery.

According to an essential feature of the present invention, the electrode according to the
15 invention comprises at least one electrode active material and an oxide electronic conductor material, preferably comprises zones of electrode active material P at least partially covered by a coating of an oxide electronic conductor material throughout the internal volume of the electrode as well as at the surface, preferably comprises zones of electrode active material P covered with a coating of an electronic conductor material, throughout the internal volume
20 of the electrode as well as at the surface, in a perfectly distributed manner.

The coating of an oxide electronic conductor material according to the invention is advantageous, of SnO_2 , ZnO doped with aluminium ($\text{ZnO}:\text{Al}$, preferably having a molar ratio Zn: Al between 1: 0.015 and 1: 0.05), of MoO_3 , SrMoO_3 , In_2O_3 , Ga_2O_3 , or indium tin oxide. The thickness of the coating of an oxide electronic conductor material throughout the
25 internal volume of the electrode is advantageously less than 10 nm, preferably less than 7 nm, preferably less than 5 nm, more preferably between 5 nm and 3 nm and still more preferably less than 3 nm. This oxide electronic conductor material can be produced from at least one precursor of said oxide electronic conductor material, in particular from at least one liquid precursor of said oxide electronic conductor material.

30 This thickness is measured by any appropriate technique, in particular by transmission electron microscopy.

More particularly, as explained above, the method according to the invention, which must include a step of forming a layer from agglomerated nanoparticles of electrode material (active material) and from at least one oxide electronic conductor material precursor, causes
35 the nanoparticles to "weld" together naturally in order 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 application of a surface treatment, by gaseous or liquid means, or by impregnation which enters the depth of the open porous structure of the layer.

A first object of the invention is a method for producing a porous electrode, in particular for electrical energy storage or production devices, such as a battery, said electrode being a porous layer comprising at least one electrode active material P and an oxide electronic conductor material deposited on a substrate, said electrode being free of binder, having a porosity between 25% and 60% by volume, preferably between 25% and 50%, and pores of average diameter less than 100 nm, said production method being characterised in that it comprises:

- (a) providing a substrate, at least one oxide electronic conductor material precursor, and a colloidal suspension or a paste comprising aggregates or agglomerates of primary nanoparticles, at least one electrode active material P, of primary median diameter D_{50} between 2 nm and 400 nm, preferably between 2 nm and 100 nm, and more preferably between 2 nm and 60 nm, said aggregates or agglomerates having a median diameter D_{50} between 50 nm and 900 nm, and preferably between 100 nm and 800 nm, understanding that said substrate can be a substrate capable of acting as electric current collector, or being an intermediate substrate,
- (b) mixing said one or more oxide electronic conductor material precursors and said colloidal suspension or said paste comprising aggregates or agglomerates of primary nanoparticles, of at least one electrode active material P provided in step (a), so as to form a mixture,
- (c) forming a layer from the mixture obtained at the end of step (b), by a method selected from the group consisting of: electrophoresis, an additive manufacturing method, exclusion, a printing method, preferably inkjet printing or flexographic printing, a coating method, preferably doctor blade coating, roll coating, curtain coating, dip coating, or slot-die coating.
- (d) drying said layer obtained in step (c) so as to obtain a dried layer, where appropriate said dried layer is separated from its intermediate substrate after the drying step (d),
- (e) transforming the one or more oxide electronic conductor material precursors into oxide electronic conductor material, so that said dried layer comprises said oxide electronic conductor material,

- (f) consolidating said layer, by heat treatment and/or mechanical treatment, preferably by sintering, in order to obtain a porous, preferably mesoporous electrode,

it being understood that steps (e) and (f) can be carried out during the same heat treatment.

- 5 The method according to the invention can comprise, in step (e), in step (f) or between steps (e) and (f), a heat treatment of said dried layer, preferably in an oxidising atmosphere.

Advantageously, after step (f), the pores of said porous electrode are impregnated by an electrolyte. The electrolyte may comprise either a lithium salt, a potassium salt or a sodium salt, depending on the intended type of battery. The electrolyte is preferably a phase carrying

- 10 lithium ions, sodium ions or potassium ions selected from the group consisting of:

- an electrolyte composed of at least one aprotic solvent and of at least one lithium, sodium or potassium salt;
- an electrolyte composed of at least one ionic liquid and of at least lithium, sodium or potassium salt;
- 15 ○ a mixture of at least one aprotic solvent and of at least one ionic liquid and of at least one lithium, sodium or potassium salt;
- an ionic liquid polymer;
- a polymer made ionic conductor by the addition of at least one lithium, sodium or potassium salt; and
- 20 ○ a polymer made ionic conductor by the addition of a liquid electrolyte, either in the polymer phase or in the porous structure of the porous electrode,

- or by an ionic conductor polymer, preferably chosen from polyethylene oxide (PEO), polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(propylene carbonate) (PPC), poly(ethylene carbonate) (PEC), poly(vinyl carbonate) (PVC), polyvinylidene fluoride (PVDF), polypropylene glycol (PPG), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), polydimethylsiloxane (PDMS), poly(ϵ -caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC).
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- The phase carrying lithium ions can comprise a mixture of several ionic liquids. Advantageously, the ionic liquid can be a cation of type 1-ethyl-3-methylimidazolium (also called EMI⁺) and/or n-propyl-n-methylpyrrolidinium (also called PYR₁₃⁺) and/or n-butyl-n-methylpyrrolidinium (also called PYR₁₄⁺), combined with anions of the type bis(trifluoromethanesulfonyl)imide (TFSI⁻) and/or bis(fluorosulfonyl)imide (FSI⁻). In order to form an electrolyte, a lithium salt such as LiTFSI can be dissolved in the ionic liquid which acts as solvent, or in a solvent such as γ -butyrolactone. γ -butyrolactone prevents the
- 35 crystallisation of ionic liquids providing a larger operating temperature range thereof, in

particular at low temperature. The phase carrying sodium or potassium ions can comprise a mixture of several ionic liquids. The ionic liquid can be as described above. In order to form an electrolyte, a sodium salt such as NaTFSI can be used instead of LiTFSI in a sodium-ion battery, or a potassium salt such as KTFSI can be used instead of LiTFSI, in a potassium-ion battery. The phase carrying lithium ions, sodium or potassium ions can comprise an ionic liquid polymer, such as poly(1-vinyl-3-alkyl-imidazolium) or else a poly(1-vinyl-N-alkyl-pyrrolidinium).

In step (c), a layer can be formed on one or both faces of the substrate.

Advantageously, when said substrate is an intermediate substrate, said layer of said intermediate substrate is separated in step (d) after drying of said layer, in order to form a porous plate, in particular after consolidation.

Advantageously, when said substrate is an intermediate substrate, after (f), an electrically conductive sheet is provided, covered on at least one face, respectively on its two faces, with a thin film of conductive adhesive, then at least one porous plate is bonded on one face, preferably on each of the faces, of the electrically conductive sheet, so as to obtain a plate or porous, preferably mesoporous, layer on a substrate capable of acting as a current collector. In the present application, the terms "porous layer" and "porous plate" are interchangeable.

Advantageously, step (b), is performed by placing the colloidal suspension or the paste provided in step (a), comprising aggregates or agglomerates of primary nanoparticles of at least one electrode active material P, in contact with a liquid phase containing at least one precursor of said oxide electronic conductor material, and in that said transformation of the one or more oxide electronic conductor material precursors into an oxide electronic conductor material during step (e) is carried out by heat treatment, such as calcination, preferably carried out in air or in an oxidising atmosphere.

Advantageously, said one or more oxide electronic conductor material precursors are chosen from organic salts containing one or more metallic elements capable, after heat treatment such as calcination, of forming an oxide electronic conductor, and said transformation into electronic conductor material is a heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere.

These organic salts are, preferably, chosen from:

- an alcoholate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor,

- a nitrate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor,

5 - an oxalate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor, and

- an acetate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor,

10 and/or preferably, the metallic element is chosen from tin, zinc, indium, gallium, molybdenum or a mixture of two or three or four or five of these elements.

The metallic element can comprise at least one dopant element.

Advantageously, said porous layer obtained at the end of step (f) has a specific surface area between $10 \text{ m}^2/\text{g}$ and $500 \text{ m}^2/\text{g}$ and/or a thickness between $2 \text{ }\mu\text{m}$ and $400 \text{ }\mu\text{m}$,
15 preferably between $2 \text{ }\mu\text{m}$ and $300 \text{ }\mu\text{m}$, more preferably between $3 \text{ }\mu\text{m}$ and $200 \text{ }\mu\text{m}$.

Advantageously, said porous electrode obtained at the end of step (f) has a specific surface area between $10 \text{ m}^2/\text{g}$ and $500 \text{ m}^2/\text{g}$ and/or a thickness between $2 \text{ }\mu\text{m}$ and $20 \text{ }\mu\text{m}$ when the substrate is a substrate capable of acting as electric current collector.

Advantageously, said porous electrode obtained at the end of step (f) has a specific surface
20 area between $10 \text{ m}^2/\text{g}$ and $500 \text{ m}^2/\text{g}$ and/or a thickness between $25 \text{ }\mu\text{m}$ and $500 \text{ }\mu\text{m}$, preferably between $50 \text{ }\mu\text{m}$ and $400 \text{ }\mu\text{m}$, when the substrate is an intermediate substrate.

Advantageously, when said colloidal suspension or paste provided in step (a) comprises organic additives, such as ligands, stabilisers, binders or residual organic solvents, the heat
25 treatment is carried out, preferably in an oxidising atmosphere, of said dried layer obtained at the end of step (d), or of said porous plate, it being understood that this heat treatment and steps (e) and/or (f) can be carried out during a same heat treatment step.

Advantageously, said electrode active material P is selected from the group (A) consisting of:

30 ○ 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 a mixture of these compounds and where $0 < x < 0.4$, LiFeO_2 , $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$,
35 $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ with $0 \leq x < 0.15$, $\text{LiNi}_{1/x}\text{Co}_{1/y}\text{Mn}_{1/z}\text{O}_2$ with $x+y+z=10$;

- $\text{Li}_x\text{M}_y\text{O}_2$ where $0.6 \leq y \leq 0.85$; $0 \leq x+y \leq 2$; and M is chosen from Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Sn, and Sb or a mixture of these elements; $\text{Li}_{1.20}\text{Nb}_{0.20}\text{Mn}_{0.60}\text{O}_2$;
 - $\text{Li}_{1+x}\text{Nb}_y\text{Me}_z\text{A}_p\text{O}_2$ where Me is at least one transition metal chosen 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, 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 $0 \leq p \leq 0.2$;
 - $\text{Li}_x\text{Nb}_{y-a}\text{Na}_z\text{M}_{z-b}\text{P}_b\text{O}_{2-c}\text{F}_c$ 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 chosen in the group consisting of Ti, Ta, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Zr, Y, Mo, Ru, Rh, Ce and Sb;
 - $\text{Li}_{1.25}\text{Nb}_{0.25}\text{Mn}_{0.50}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.40}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Fe}_{0.40}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.43}\text{Ni}_{0.27}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.43}\text{Co}_{0.27}\text{O}_2$; $\text{Li}_{1.4}\text{Nb}_{0.2}\text{Mn}_{0.53}\text{O}_2$;
 - $\text{Li}_x\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_y$ where $0.00 \leq x \leq 1.52$; $1.07 \leq y < 2.4$; $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$;
 - $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ 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 $0 \leq z$;
 - 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 $M = \text{Fe, Co, Ni}$ or a mixture of these different elements, LiMPO_4F with $M = \text{V, Fe, T}$ or a mixture of these different elements; the phosphates of formula $\text{LiMM}'\text{PO}_4$, with M and M' ($M \neq M'$) selected from Fe, Mn, Ni, Co, V such as $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ and where $0 < x < 1$;
 - $\text{Fe}_{0.9}\text{Co}_{0.1}\text{OF}$; FeF_3 ; LiMSO_4F with $M = \text{Fe, Co, Ni, Mn, Zn, Mg}$;
 - 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 , $\text{Li}_x\text{V}_2\text{O}_5$ 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 oxysulfides and lithium $\text{Li}_x\text{TiO}_y\text{S}_z$ 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 $0 < x \leq 1$;
- or in the group (B) consisting of:
- transition metal oxides:
 - $\text{Na}_x\text{MO}_{2+z}$ with M chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;
 - $\text{Na}_x\text{M}_{u/2}\text{M}'_{v/2}\text{O}_{2+z}$ with $u + v = 2$ and M, M' chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;

- $\text{Na}_x\text{M}_{u/3}\text{M}'_{v/3}\text{M}''_{w/3}\text{O}_{2+z}$ with $u + v + w = 3$ and M, M', M'' chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;
 - $\text{Na}_x\text{Mn}_y\text{Ni}_z\text{Fe}_{0.1}\text{Mg}_{0.1}\text{O}_2$ with $0.67 \leq x \leq 1.0$; $0.5 \leq y \leq 0.7$ and $0.1 \leq z \leq 0.3$;
 - Prussian blue and/or Prussian blue analogues, known by the abbreviation PBA:
 - $\text{Na}_x\text{M}^1[\text{M}^{2'}(\text{CN})_6]_y \cdot n\text{H}_2\text{O}$, M^1 being a transition metal or a transition metal alloy, $\text{M}^{2'}$ being a transition metal, the transition metal and the transition metal alloy being chosen from the Fe, Ni, Co and Mn, with $0 \leq x \leq 2$; $y \leq 1$ and $0 \leq n \leq 12$;
 - polyanionic compounds:
 - $\text{Na}_x\text{M}_2(\text{XO}_4)_3$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$, such as $\text{Na}_3\text{V}_2(\text{PO}_4)_3$;
 - $\text{Na}_x\text{M}_3(\text{XO}_4)_2(\text{X}_2\text{O}_7)$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;
 - $\text{Na}_x\text{M}(\text{X}_2\text{O}_7)$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;
 - $\text{Na}_x\text{M}_2(\text{XO}_4)_2\text{F}_3$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;
 - $\text{Na}_x\text{M}_2(\text{XO}_4)_2\text{F}_{3-y}\text{O}_y$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $0.07 \leq y \leq 0.12$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;
 - $\text{Na}_x\text{M}_2\text{O}_2(\text{XO}_4)_2\text{F}$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;
 - Na_xMXO_4 with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;
- or in the group (C) consisting of:
- transition metal oxides:
 - $\text{K}_x\text{MO}_{2+z}$ with M chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;
 - $\text{K}_x\text{M}_{u/2}\text{M}'_{v/2}\text{O}_{2+z}$ with $u + v = 2$ and M, M' chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;

- $K_x M_{u/3} M'_{v/3} M''_{w/3} O_{2+z}$ with $u + v + w = 3$ and M, M', M'' chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;
 - $K_x Mn_y Ni_z Fe_{0.1} Mg_{0.1} O_2$ with $0.67 \leq x \leq 1.0$; $0.5 \leq y \leq 0.7$ and $0.1 \leq z \leq 0.3$;
- Prussian blue and/or Prussian blue analogues, known by the abbreviation PBA:
 - $K_x M^1 [M^2 (CN)_6]_y \cdot nH_2O$, M^1 being a transition metal or a transition metal alloy, M^2 being a transition metal, the transition metal and the transition metal alloy being chosen from the Fe, Ni, Co and Mn, with $0 \leq x \leq 2$; $y \leq 1$ and $0 \leq n \leq 12$;
- polyanionic compounds:
 - $K_x M_2 (XO_4)_3$ with $0 < x \leq 4$, $M = V, Fe, Cr, Mn, Co, Ni$ or Sc and $X = P, S, As, Si, Mo$ or W, such as $Na_3 V_2 (PO_4)_3$;
 - $K_x M_3 (XO_4)_2 (X_2 O_7)$ with $0 < x \leq 4$, $M = V, Fe, Cr, Mn, Co, Ni$ or Sc and $X = P, S, As, Si, Mo$ or W;
 - $K_x M (X_2 O_7)$ with $0 < x \leq 4$, $M = V, Fe, Cr, Mn, Co, Ni$ or Sc and $X = P, S, As, Si, Mo$ or W;
 - $K_x M_2 (XO_4)_2 F_3$ with $0 < x \leq 4$, $M = V, Fe, Cr, Mn, Co, Ni$ or Sc and $X = P, S, As, Si, Mo$ or W;
 - $K_x M_2 (XO_4)_2 F_{3-y} O_y$ with $0 < x \leq 4$, $M = V, Fe, Cr, Mn, Co, Ni$ or Sc and $0.07 \leq y \leq 0.12$ and $X = P, S, As, Si, Mo$ or W;
 - $K_x M_2 O_2 (XO_4)_2 F$ with $0 < x \leq 4$, $M = V, Fe, Cr, Mn, Co, Ni$ or Sc and $X = P, S, As, Si, Mo$ or W;
 - $K_x MXO_4$ with $0 < x \leq 4$, $M = V, Fe, Cr, Mn, Co, Ni$ or Sc and $X = P, S, As, Si, Mo$ or W.

Advantageously, said above-mentioned electrode active material P is used to produce a cathode.

Advantageously, said electrode active material P is an selected from the group (D) consisting of:

- $Li_4 Ti_5 O_{12}$, $Li_4 Ti_{5-x} M_x O_{12}$ with $M = V, Zr, Hf, Nb, Ta$ and $0 \leq x \leq 0.25$;
- niobium oxides and mixed oxides of niobium with titanium, germanium, cerium or tungsten, and preferably in the group consisting of:

- $\text{Nb}_2\text{O}_{5\pm\delta}$, $\text{Nb}_{12}\text{WO}_{33\pm\delta}$, $\text{Nb}_{14}\text{W}_3\text{O}_{44\pm\delta}$, $\text{Nb}_{18}\text{W}_{16}\text{O}_{93\pm\delta}$, $\text{Nb}_{16}\text{W}_5\text{O}_{55\pm\delta}$ with $0 \leq \delta \leq 2$, LiNbO_3 ,
- $\text{TiNb}_2\text{O}_{7\pm\delta}$, $\text{Li}_w\text{TiNb}_2\text{O}_7$ 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 chosen in the group consisting 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 being able to be identical or different from one another, and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $0 \leq \delta \leq 0.3$;
- $\text{La}_x\text{Ti}_{1-2x}\text{Nb}_{2+x}\text{O}_7$ where $0 < x < 0.5$;
- $\text{M}_x\text{Ti}_{1-2x}\text{Nb}_{2+x}\text{O}_{7\pm\delta}$
 - wherein M is an element for which the oxidation value is +III, more particularly M is at least one of the elements chosen in the group consisting of Fe, Ga, Mo, Al, B, and where $0 < x \leq 0.20$ and $-0.3 \leq \delta \leq 0.3$;
 $\text{Ga}_{0.10}\text{Ti}_{0.80}\text{Nb}_{2.10}\text{O}_7$; $\text{Fe}_{0.10}\text{Ti}_{0.80}\text{Nb}_{2.10}\text{O}_7$;
- $\text{M}_x\text{Ti}_{2-2x}\text{Nb}_{10+x}\text{O}_{29\pm\delta}$
 - wherein M is an element for which the oxidation value is +III, more particularly M is at least one of the elements chosen in the group consisting of Fe, Ga, Mo, Al, B, and where $0 < x \leq 0.40$ and $-0.3 \leq \delta \leq 0.3$;
- $\text{Ti}_{1-x}\text{M}^1_x\text{Nb}_{2-y}\text{M}^2_y\text{O}_{7-z}\text{M}^3_z$ 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
 - M^1 and M^2 are each at least one element chosen in the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs and Sn,
 - M^1 and M^2 being able to be identical or different from one another,
 - M^3 is at least one halogen,
 - and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
- $\text{TiNb}_2\text{O}_{7-z}\text{M}^3_z$ or $\text{Li}_w\text{TiNb}_2\text{O}_{7-z}\text{M}^3_z$ wherein M^3 is at least one halogen, preferably chosen from F, Cl, Br, I or a mixture of these, with $0 \leq z \leq 0.3$ and $0 < w \leq 0.5$;
- $\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$, $\text{Li}_w\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$, $\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$, $\text{Li}_w\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$ wherein
 - M^1 is at least one element chosen in the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs and Sn;
 - $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
- $\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$, $\text{Li}_w\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$, $\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$, $\text{Li}_w\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$, wherein

- M^1 and M^2 are each at least one element chosen in the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs, Ce and Sn,
 - M^1 and M^2 being able to be identical or different from one another,
 - and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
 - TiO_2 ; TiO_xN_y with $x < 2$ and $0 < y < 0.2$;
 - LiSiTON, the oxynitrides based on tin and silicon, and more particularly the formulation $SiSn_{0.87}O_{1.20}N_{1.72}$ and their lithiated forms;
 - nitrides and oxynitrides of type MO_xN_y , where M is at least one element chosen from Ge, Si, Sn, Zn, Co, Ni, Cu, Fe or a mixture of one or more of these elements, and where $x \geq 0$ and $y \geq 0.3$;
 - $Li_{3-x}M_xN$ with M is at least one element chosen from Cu, Ni, Co or a mixture of one or more of these elements and $0 \leq x \leq 1$;
 - $Li_{3-x}M_xN$ with M being cobalt (Co) and $0 \leq x \leq 0.5$; $Li_{3-x}M_xN$ with M being nickel (Ni) and $0 \leq x \leq 0.6$; $Li_{3-x}M_xN$ with M being copper (Cu) and $0 \leq x \leq 0.3$;
 - lithiated iron phosphate (of typical formula $LiFePO_4$);
 - mixed oxynitrides of silicon and tin, of typical formula $Si_aSn_bO_yN_z$ with $a > 0$, $b > 0$, $a+b \leq 2$, $0 < y \leq 4$, $0 < z \leq 3$, also called SiTON, and in particular $SiSn_{0.87}O_{1.2}N_{1.72}$; as well as oxynitride carbides of typical formula $Si_aSn_bC_cO_yN_z$ with $a > 0$, $b > 0$, $a+b \leq 2$, $0 < c < 10$, $0 < y < 24$, $0 < z < 17$;
 - nitrides of type Si_xN_y , in particular with $x=3$ and $y=4$; Sn_xN_y , in particular with $x=3$ and $y=4$, Zn_xN_y , in particular with $x=3$ and $y=2$; $Li_{3-x}M_xN$ with $0 \leq x \leq 0.5$ for $M=Co$, $0 \leq x \leq 0.6$ for $M=Ni$, $0 \leq x \leq 0.3$ for $M=Cu$; $Si_{3-x}M_xN_4$ with $M=Co$ or Fe and $0 \leq x \leq 3$.
 - oxides SnO_2 , SnO , Li_2SnO_3 , $SnSiO_3$, Li_xSiO_y with $x \geq 0$ and $2 > y > 0$, $Li_4Ti_5O_{12}$, $TiNb_2O_7$, Co_3O_4 , $SnB_{0.6}P_{0.4}O_{2.9}$ and TiO_2 ,
 - Si, Sn, SiO_2 , SnO_2 , SiN, SnN and the mixtures thereof,
 - composite oxides $TiNb_2O_7$ comprising between 0% and 10% by mass of carbon, the carbon preferably being chosen from graphene and carbon nanotubes;
- or in the group (E) consisting of:
- alloys based on Si, Ge, Sn, Sb, Bi or P and the alloys of these various compounds
 - MXenes. MXenes are a class of two-dimensional materials with stoichiometry of type $M_{n+1}X_nT_x$ with M a transition metal, preferably chosen from Sc, Ti, V, Cr, Y, Zr, Nb, Mo, Hf, Ta, W and X is chosen from C and/or N and T a surface termination chosen from F, Cl, I, Br, O, S, Se, Te, OH, NH_2 , $1 \leq n \leq 4$

- conversion anode materials such as
 - o oxides of type $G_2Ti_3O_7$, $G_4Ti_5O_{12}$, $GTi_2(PO_4)_3$, G being Na or K
 - o oxides, sulfides, selenides and phosphides of the following elements and their alloys: Si, Ge, Sn, Sb, Bi.

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Advantageously, said above-mentioned electrode active material P is used to produce an anode.

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Another object of the invention is a porous electrode, in particular for electrical energy storage or production devices, characterised in that it comprises at least one electrode active material P and an oxide electronic conductor material, in that it is free of binder, in that it has a porosity between 25% and 60% by volume, preferably between 25% and 50%.

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Another object of the invention is a porous electrode that can be obtained by the method according to the invention. Another object of the invention is a porous electrode that can be obtained by the method according to the invention, characterised in that the porous electrode comprises at least one electrode active material P and an oxide electronic conductor material, in that it is free of binder, and in that it has a porosity between 25% and 60% by volume, preferably between 25% and 50%.

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Another object of the invention is a method for producing an electrical energy storage or production device, preferably selected from the group consisting of: capacitors, supercapacitors, hybrid supercapacitors, such as the lithium-ion hybrid supercapacitors, sodium-ion hybrid supercapacitors, potassium-ion hybrid supercapacitors, photovoltaic cells, the photo-electrochemical cells and batteries such as lithium-ion batteries, sodium-ion batteries, potassium-ion batteries, implementing the method for producing a porous electrode according to the invention or using a porous electrode according to the invention. Another object of the invention is a method for producing an electrical energy storage or production device, such as battery, a capacitor, a supercapacitor, a hybrid supercapacitor such as a lithium-ion hybrid supercapacitor, a sodium-ion hybrid supercapacitor, a potassium-ion hybrid supercapacitor, a photochemical cell, a photovoltaic cell, and in particular a method for producing a lithium-ion, sodium-ion, or potassium-ion battery, implementing the method for producing a porous electrode according to the invention.

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Advantageously, when the electrical energy storage or production device is a lithium-ion hybrid supercapacitor or a lithium-ion battery, the production method of the cathode uses

the electrode active material P chosen in group (A) or the production method of the anode uses the electrode active material P chosen in group (D).

Advantageously, when the electrical energy storage or production device is a sodium-ion hybrid supercapacitor or a sodium-ion battery, the production method of the cathode uses

5 the electrode active material P chosen in group (B) or the production method of the anode uses the electrode active material P chosen in group (E) (where appropriate, G being Na).

Advantageously, when the electrical energy storage or production device is a potassium-ion hybrid supercapacitor or a potassium-ion battery, the production method of the cathode

10 uses the electrode active material P chosen in group (C) or the production method of the anode uses the electrode active material P chosen in group (E) (where appropriate, G being K).

Advantageously, in the method for producing a lithium-ion battery, the method for producing a porous electrode is implemented in order to produce a cathode with the electrode active

15 material P chosen in group (A) or the method for producing an anode it is implemented with the electrode active material P chosen in group (D).

In particular, this method is well suited to the production of batteries, and generally, the battery according to the invention can be designed and sized as a surface-mounted

20 component (a technology commonly abbreviated to "SMT" for surface-mount technology), so as to be compatible with the methods for manufacturing microelectronics, in particular with the robotic methods for filling electronic boards, known by the term "pick and place".

Advantageously, said porous electrode is impregnated by an electrolyte, preferably by a phase carrying lithium ions, sodium ions or potassium ions selected from the group

25 consisting of:

- an electrolyte composed of at least one aprotic solvent and of at least one lithium, sodium or potassium salt;
- an electrolyte composed of at least one ionic liquid and of at least lithium, sodium or potassium salt;
- 30 ○ a mixture of at least one aprotic solvent and of at least one ionic liquid and of at least one lithium, sodium or potassium salt;
- an ionic liquid polymer;
- a polymer made ionic conductor by the addition of at least one lithium, sodium or potassium salt; and
- 35 ○ a polymer made ionic conductor by the addition of a liquid electrolyte, either in the polymer phase, or in the porous structure,

or by an ionic conductor polymer, preferably chosen from polyethylene oxide (PEO), polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(propylene carbonate) (PPC), poly(ethylene carbonate) (PEC), poly(vinyl carbonate) (PVC), polyvinylidene fluoride (PVDF), polypropylene glycol (PPG), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), polydimethylsiloxane (PDMS), poly(ϵ -caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC).

Another object of the invention is an electrical energy storage or production device that can be obtained by the method according to the invention, preferably a battery, preferably a lithium-ion, sodium-ion or potassium-ion battery that can be obtained by the method according to the invention.

Advantageously, the electrical energy storage or production device according to the invention is a capacitor, supercapacitor, hybrid supercapacitor such as a lithium-ion hybrid supercapacitor, a sodium-ion hybrid supercapacitor, a potassium-ion hybrid supercapacitor, a photovoltaic cell, a photochemical cell, or a battery such as a lithium-ion battery, a sodium-ion battery or a potassium-ion battery.

Advantageously, when the electrical energy storage or production device is a lithium-ion hybrid supercapacitor or a lithium-ion battery, the electrode active material P is chosen in group (A) for the cathode active material and/or in group (D) for the anode active material. Advantageously, when the electrical energy storage or production device is a sodium-ion hybrid supercapacitor or a sodium-ion battery, the electrode active material P is chosen in group (B) for the cathode active material and/or in the group (E) for the anode active material (where appropriate, G being Na).

Advantageously, when the electrical energy storage or production device is a potassium-ion hybrid supercapacitor or a potassium-ion battery, the electrode active material P is chosen in group (C) for the cathode active material and/or in the group (E) for the anode active material (where appropriate, G being K).

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The method according to the invention is particularly suitable for producing a porous electrode having a thickness greater than 1 μm , or even greater than 3 μm , while ensuring a low series resistance of the battery.

Another object of the invention is an electrical energy storage or production device, such as a battery, capacitor, supercapacitor, photovoltaic cell or photochemical cell, comprising a

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porous electrode according to the invention or that can be obtained by the method according to the invention.

Detailed description of the invention

5 1. Definitions

The present invention relates to a porous electrode, for which the accessible surface, i.e. the outer surface of the electrode, as well as the accessible interior pores of the electrode, is covered with an oxide electronic conductor material. The term "oxide electronic conductor" comprises oxide electronic conductors and oxide electronic semiconductors.

10 In the context of the present document, the size of a particle is defined by its largest dimension. The term "nanoparticle" shall mean any particle or object of nanometric size having at least one of its dimensions less than or equal to 400 nm.

The term "ionic liquid" shall mean any liquid salt that is able to transport electricity, distinguished from the set of molten salts by a melting temperature less than 100°C. Some
15 of these salts remain liquid at ambient temperature and do not solidify, even at very low temperature. Such salts are called "ambient temperature ionic liquids".

The term "electrolyte" shall mean any ionic conductive substance due to the presence of mobile ions; it can be solid without a liquid phase, or liquid. These ions are preferably Li⁺, Na⁺ or K⁺. A liquid electrolyte can be in the form of a gel. In order to galvanically separate
20 the electrodes, the electrolytes are electronically insulating.

The term "mesoporous" materials shall mean any solid which has, within its structure, pores termed "mesopores" having a size intermediate between that of micropores (width less than 2 nm) and that of macropores (width greater than 50 nm), namely of size between 2 nm and 50 nm. This terminology corresponds to that adopted by the IUPAC (International Union for
25 Pure and Applied Chemistry), which is a reference for a person skilled in the art. The term "nanopore" is therefore not used here, even if the mesopores as defined above have nanometric dimensions within the meaning of the definition of nanoparticles, it being understood that pores of size less than those of mesopores are called "micropores" by a person skilled in the art.

30 A presentation of the concepts of porosity (and of the terminology which has just been explained above) is given in the article "Texture des matériaux pulvérulents ou poreux" (Texture of powdery or porous materials) by F. Rouquerol et al., published in the collection "Techniques de l'Ingénieur" (Techniques for the Engineer), treaties, Analyse et Caractérisation (Analysis and Characterisation), booklet P 1050; this article also describes
35 the techniques for characterising porosity, in particular the BET method.

Within the meaning of the present invention, the term "porous layer" means a layer which has pores. The term "mesoporous layer" means a layer which has mesopores. In these layers, the pores and mesopores make a significant contribution to the total porous volume; this state of affairs is manifest by the expression "Porous/mesoporous layer with porosity greater than X% by volume" used in the present description.

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

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

2. Preparation of nanoparticle suspensions

The porous electrodes according to the invention are formed from a colloidal suspension of clusters and/or agglomerates of nanoparticles or a paste.

In a still more preferred embodiment of the invention the nanoparticles are prepared directly with their primary size by precipitation, Pechini synthesis, spray pyrolysis, hydrothermal or solvothermal synthesis. Hydrothermal or solvothermal synthesis can be used to obtain NANOPARTICLES preferably nanoparticles, with a very narrow size distribution, known as "monodispersed nanoparticles". The size of these non-aggregated or non-agglomerated nanopowders/nanoparticles is called the primary size. It is typically between 2 nm and 400 nm, preferably between 2 nm and 100 nm, and more preferably between 2 nm and 60 nm and is advantageously between 10 nm and 50 nm, preferably between 10 nm and 30 nm; this promotes, during subsequent method steps, the formation of an interconnected electronic and ionic conduction mesoporous network, through the phenomenon of "necking". Additives, such as binders, can also be added to the suspension of nanoparticles (clusters and/or agglomerates of nanoparticles, understanding that these clusters are also in the form of nanoparticles) in order to facilitate the production of deposits or green sheets, in particular thick deposits without cracks.

A layer of at least one oxide electronic conductor material precursor is formed, by any appropriate means, on these preferably monodispersed aggregates and/or agglomerates of primary nanoparticles of at least one electrode active material P.

3. A mixture comprising at least one oxide electronic conductor material precursor and a colloidal suspension or paste comprising aggregates and/or agglomerates of primary particles, of at least one electrode active material P - Formation of a layer of at least one oxide electronic conductor material precursor on the aggregates and/or agglomerates of primary nanoparticles of at least one electrode active material P.

Highly advantageously, the layer of oxide electronic conductor material can be obtained in various ways and by any appropriate means, in particular by placing the colloidal suspension, paste comprising aggregates or agglomerates of primary nanoparticles of at least one electrode active material P, in contact with a liquid phase containing at least one oxide electronic conductor material precursor following the transformation of said or one or more precursors of an electronic conductor material into electronic conductor material.

More generally, with the techniques for producing the coating of at least one oxide electronic conductor material precursor indicated here, only the accessible surfaces of the aggregates or agglomerates of primary nanoparticles of at least one electrode active material P are covered.

The formation of a layer of at least one oxide electronic conductor material precursor on the aggregates and/or agglomerates of the suspension or paste is advantageously carried out in the presence of complexing agents, such as polyvinylpyrrolidone (PVP), so as to facilitate the complexing of the one or more precursors at the surface of the aggregates/agglomerates.

This method is simple, quick and easy to implement. Advantageously, said one or more precursors of the electronic conductor material are chosen from organic salts containing one or more metallic elements capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor.

The oxide electronic conductor can optionally comprise at least one dopant element. These metallic elements, preferably metallic cations, can advantageously be chosen from tin, zinc, indium, gallium, molybdenum or a mixture of two or three or four or five of these elements.

The organic salts are preferably chosen from:

- an alcoholate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor,
- a nitrate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor,

- an oxalate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor, and
- an acetate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor.

In order to obtain a layer of an electronic conductor material, preferably an oxide electronic conductor material, from an alcoholate, a nitrate, an oxalate or an acetate, on aggregates or agglomerates of primary nanoparticles of at least one electrode active material P, the colloidal suspension or the paste comprising said aggregates or agglomerates of nanoparticles can be placed in contact with a solution rich in precursor of the desired electronic conductor material.

It is the mixture of this colloidal suspension or paste comprising aggregates or agglomerates of primary nanoparticles of an electrode active material P and of at least one oxide electronic conductor material precursor, which is then used for producing a porous dried layer and an electrode according to the invention. The mixture of this colloidal suspension or paste comprising aggregates or agglomerates of primary nanoparticles of an electrode active material P and of at least one oxide electronic conductor material precursor is hereinafter called a "mixture according to the invention". Advantageously, the mixture according to the invention is in the form of a colloidal suspension or a paste (ink).

4. Production of a porous layer

The method for producing an electrode according to the invention involves the application of a mixture comprising the one or more oxide electronic conductor material precursors and the colloidal suspension or paste comprising aggregates or agglomerates of primary nanoparticles of at least one electrode active material P, on a substrate in order to form a layer, then drying said layer in order to obtain a porous layer. This sequence comprising the application of this mixture on a substrate in order to form a layer and its drying can be repeated several times in order to increase the thickness of the porous layer. The final thickness of this porous layer is advantageously less than or equal to 5 mm, preferably between approximately 1 μm and approximately 500 μm . The thickness of this porous layer is advantageously less than 500 μm , preferably between approximately 2 μm and approximately 400 μm , more preferably between 2 μm and 300 μm , still more preferably between 3 μm and 200 μm . In general, the mixture according to the invention, in the form

of a colloidal suspension or paste, is deposited on a substrate by any appropriate technique and, in particular, by electrophoresis, extrusion, additive manufacturing (or "robocasting"), inkjet printing, spraying, flexographic printing, by a coating method, preferably using a blade (known by the term "doctor blade" or "tape casting"), by roll coating, curtain coating, extrusion through a slot-die, or dip-coating.

In order that the mixture according to the invention, has a viscosity suitable for the coating techniques usually employed for the production of electrodes, and can also be deposited on a substrate, it is advantageous to use the mixture according to the invention in the form of a colloidal suspension or paste having a solids content less than 30% by mass.

According to the findings of the applicant, with an average diameter of the aggregates or agglomerates of nanoparticles between 50 nm and 900 nm, preferably between 100 nm and 800 nm (more preferably between 100 nm and 400 nm), during subsequent method steps, a mesoporous layer is obtained having an average diameter of the mesopores between 2 nm and 100 nm.

According to the invention, the porous layer can be deposited by the ink jet printing method or by a coating method, and in particular dip-coating, roll coating, curtain coating, slot-die coating, or else by doctor blade coating, and this from a mixture according to the invention in the form of a rather concentrated suspension comprising at least one oxide electronic conductor material precursor and aggregates or agglomerates of nanoparticles of the active material P.

The porous electrode layer can also be deposited by electrophoresis, but then a mixture according to the invention is advantageously used in the form of a less concentrated suspension comprising at least one oxide electronic conductor material precursor and agglomerates of nanoparticles of the active material P.

The methods for depositing a mixture according to the invention by electrophoresis, extrusion, additive manufacturing, dip coating, inkjet, roll coating, curtain coating, doctor blade or slot-die coating are methods that are simple, safe, easy to implement and industrialise, and enabling a homogeneous final porous layer to be obtained. Deposition by electrophoresis makes it possible to deposit layers uniformly on large surfaces with high deposition speeds. The coating techniques, in particular those mentioned above, can simplify the management of baths compared with electrophoresis deposition techniques, since the suspension is not depleted of particles during the deposition. Deposition by inkjet printing enables localised deposits.

Thick, porous layers, preferably having a thickness between 50 and 400 μm , can be produced in a single step by roll coating, curtain coating, slot-die coating, or by doctor blade coating (i.e. with a blade) or else by extrusion.

The technique for depositing the mixture according to the invention in the form of a colloidal suspension or paste (ink), and the performance of the deposition method must be compatible with the viscosity of the colloidal suspension or paste (ink) used, and vice versa. The substrate is advantageously an intermediate substrate or a substrate that can act as
 5 current collector.

4.1 Substrate capable of acting as current collector

In a first embodiment, said substrate is a substrate capable of acting as electric current collector and is advantageously compatible with the heat treatments used in the method
 10 according to the invention. The substrate can advantageously be a metal substrate or a substrate made of electronic conductor carbon, in particular based on graphite, graphene and/or carbon nanotubes. Said substrate on which the mixture according to the invention is deposited in the form of a colloidal suspension or paste (ink) ensures the current collector function for the electrode. The mixture according to the invention in the form of a colloidal
 15 suspension or a paste (ink) can be deposited on one or two faces of the substrate, in particular by the above indicated deposition techniques.

The current collector in electrochemical devices using electrodes according to the invention can be a substrate that is stable in the range of potential operation of the electrochemical device. Inside batteries employing electrodes according to the invention, the current
 20 collector must be a substrate that is stable in a potential range, preferably between 2.5 V and 5 V for the cathode, and between 0 V and 2.5 V for the anode, relative to the potential of the lithium. Advantageously, a metal substrate is chosen, for example a metal strip (i.e. a laminated metal sheet). The substrate can be made, in particular, of tungsten, molybdenum, chromium, titanium, tantalum, zirconium, niobium, stainless steel, or an alloy
 25 of two or more of these materials. Such metallic substrates are rather expensive and can significantly increase the cost of the battery. Tungsten, molybdenum, chromium, titanium, tantalum, zirconium, niobium, stainless steel and their alloys are particularly resistant to high-temperature heat treatments; they are thus particularly well suited as electrode substrates which can be sintered. The reason for using these substrates that are resistant
 30 to heat treatments is to be able to sinter the, preferably thin, deposits directly on the substrate.

It is also possible to cover this substrate that is capable of acting as electric current collector, with a conductive or semi-conductive oxide before depositing the mixture according to the invention in the form of a colloidal suspension or paste (ink), which makes it possible, in
 35 particular, to protect the less noble substrates, such as copper, nickel, aluminium and carbon, in particular in the form of graphite. These less noble substrates can thus be used

as electrode substrates, in particular due to their cost. It may involve a conductive carbon sheet (typically of graphite), a metallic sheet, or a metallised non-metallic sheet (i.e. covered with a metal layer). The substrate is preferably chosen from strips made of copper, nickel, molybdenum, tungsten, tantalum, chromium, niobium, zirconium, titanium, and alloy strips containing at least one of these elements. Stainless steel can also be used. These substrates have the advantage of being stable over a large range of potential and resistant to heat treatments.

Copper, nickel, molybdenum and their alloys are preferably used as anode substrate. Carbon-based substrates, in particular in the form of graphite, based on alloys of nickel-chromium, stainless steels, chromium, titanium, aluminium, tungsten, molybdenum, tantalum, zirconium, niobium or alloys containing at least one of these elements are, preferably, used as electric current collector substrates for cathodes. These anodic and/or cathodic substrates can be covered or not covered by an electrochemically inert conductive layer. Such layers can be produced by depositing nitrides, carbides, graphites, gold, palladium and/or platinum.

The mixture according to the invention in the form of a colloidal suspension or paste (ink) can be deposited on one or both faces of the substrate capable of acting as current collector. The layer deposited on this substrate is then dried so as to obtain a porous layer comprising an electrode active material P, as well as at least one precursor of an active electronic conductor material.

The transformation of the one or more oxide electronic conductor material precursors into oxide electronic conductor material is then performed on this porous dried layer initially deposited on one or both faces of the substrate capable of acting as current collector.

4.2 Intermediate substrate

According to a second embodiment, the mixture according to the invention is not deposited in the form of a colloidal suspension or paste comprising an electrode active material P, as well as at least one precursor of an active material electronic conductor (ink), on a substrate capable of acting as electric current collector, but on an intermediate substrate, which is typically used in a temporary manner.

In this embodiment, the mixture according to the invention in the form of a colloidal suspension or paste (ink) is deposited on a face of the intermediate substrate, so as to be able to subsequently easily separate the layer obtained from this intermediate substrate.

In particular, it is possible to deposit, from the mixture according to the invention in the form of a suspension or paste comprising at least one oxide electronic conductor material precursor and aggregates and/or agglomerates of nanoparticles of electrode active material

P, preferably from a concentrated suspension comprising at least one oxide electronic conductor material precursor and aggregates and/or agglomerates of nanoparticles of electrode active material P (i.e. less fluid, preferably pasty), rather thick layers, termed "green sheet". These thick layers can be deposited by any appropriate means, in particular
 5 by the inkjet printing method, by extrusion, additive manufacturing, spraying, flexographic printing, a coating method, preferably doctor blade coating, roll coating, curtain coating, by slot-die extrusion, or by dipping.

The methods for depositing nanoparticles, by the dip coating method, by the inkjet printing method by roll coating, curtain coating, slot-die coating, by extrusion, additive
 10 manufacturing, spraying, flexographic printing or doctor blade coating are simple, safe, easy to implement and industrialise methods, enabling a homogeneous deposit to be obtained. Inkjet printing allows the mixture according to the invention to be deposited in a localised manner, in the same manner as the doctor blade depositions under a mask. Thick layers can be obtained in a single step by the roll, curtain, slot-die, dipping, extrusion, additive
 15 manufacturing or doctor blade coating techniques.

Said intermediate substrate can be a flexible substrate, which can be a polymer sheet, for example polyethylene terephthalate, abbreviated as PET. In this second embodiment, the deposition step is advantageously made on one face of said intermediate substrate, in order to facilitate the later separation of the layer from its substrate. In this second embodiment,
 20 the layer is separated from its substrate after drying and before any high-temperature heat treatment. The thickness of the layer after drying, is advantageously less than or equal to 5 mm, advantageously between approximately 1 μm and approximately 600 μm . The thickness of the layer after drying is advantageously less than 500 μm , preferably, between approximately 3 μm and approximately 400 μm , more preferably between 3 μm and 300
 25 μm .

In said second embodiment, the method for producing an electrode for an electrochemical device, such as a battery, uses an intermediate substrate preferably made of polymer (such as PET) and leads to a strip referred to as "green strip". After drying, this green strip is next separated from its substrate; it then forms self-supporting plates or sheets (here, in the
 30 following, the term "plate" is used, whatever its thickness).

The transformation of the one or more oxide electronic conductor material precursors into oxide electronic conductor material is then performed on these self-supporting porous plate or sheets.

35 5. Transformation of the one or more oxide electronic conductor material precursors present in the porous dried layer into oxide electronic conductor material

The self-supporting porous dried layer or porous plate comprising an electrode active material P and at least one precursor of an active material electronic conductor is subjected to a heat treatment, preferably in air or in an oxidising atmosphere, at a sufficient temperature to transform the one or more oxide electronic conductor material precursors in question into oxide electronic conductor material. Thus zones of electrode active material P are formed, at least partially covered by a coating of the electronic conductor material, preferably a coating of an oxide electronic conductor material, more preferably SnO_2 , ZnO doped with aluminium (ZnO:Al , preferably having a molar ratio Zn: Al between 1: 0.015 and 1: 0,05), In_2O_3 , Ga_2O_3 , MoO_3 , en SrMoO_3 , , a coating comprising a mixture of two of these oxides, such as indium tin oxide corresponding to a mixture of indium oxide (In_2O_3) and tin oxide (SnO_2), a mixture of three of these oxides, a mixture of four of these oxides, a mixture of five of these oxides, or a mixture of six of these oxides, throughout the internal volume of the electrode as well as at the surface, in a perfectly distributed manner.

This heat treatment, preferably carried out in an oxidising atmosphere, can eliminate the organic constituents, i.e. perform a debinding. This heat treatment can also enable, as a function of the nature of the electrode active material P used and of the temperature employed for transforming the one or more oxide electronic conductor material precursors in question into oxide electronic conductor material, consolidating the layer or porous plate, as will be explained in detail in the following section.

With regard to the prior art and in particular a porous electrode comprising a carbon coating on and inside the pores of the electrode as described in application WO 2021/220174, the presence of zones of electrode active material P at least partially covered by a coating of the oxide electronic conductor material, preferably covered by a coating of the oxide electronic conductor material, throughout the internal volume of the electrode as well as at the surface, in a perfectly distributed manner, gives the electrode better electrochemical performance at high temperature, and significantly increases the stability of the electrode. The fact of using this singular three-dimensional structure comprising zones of electrode active material P at least partially covered by a coating of an oxide electronic conductor material throughout the internal volume of the electrode as well as at the surface, preferably comprising zones of electrode active material P covered with a coating of the oxide electronic conductor material throughout the internal volume of the electrode as well as at the surface, gives, inter alia, a better performance of the final electrode. More particularly, the presence of zones of electrode active material P at least partially covered by a coating of an oxide electronic conductor material, preferably covered with a coating of the oxide electronic conductor material throughout the internal volume of the electrode as well as at

the surface, can improve the final properties of the electrode, in particular can improve the voltage stability of the electrode and its temperature stability, and improve the electrochemical stability of the electrode, in particular when it will be in contact with a liquid electrolyte, to reduce the resistance to polarisation of the electrode, and this even when the electrode is thick. It is particularly advantageous to use an electronic conductor material in the form of an oxide, in particular of type In_2O_3 , SnO_2 , ZnO doped with aluminium ($\text{ZnO}:\text{Al}$, preferably having a molar ratio $\text{Zn}:\text{Al}$ between 1: 0.015 and 1: 0.05), Ga_2O_3 , MoO_3 , , SrMoO_3 , or a mixture of one or more of these oxides or of these doped oxides, in the volume of the electrode, when the electrode is thick, and/or the active materials of the porous layer are too resistive.

The electrode according to the invention is porous, preferably mesoporous, and its specific surface area is advantageously large. The increase in the specific surface area of the electrode multiplies the exchange surface areas and consequently the power of the battery, but it also accelerates the parasite reactions. The presence of these electronic conductor coatings in the form of an oxide in the volume of the electrode will enable these parasite reactions to be blocked.

Furthermore, due to the fact of the very large specific surface area, the effect of these electronic conductor coatings in oxide form on the electronic conductivity of the electrode will be much more pronounced than in the case of a conventional electrode, where the specific surface area is less, and this even if the conductor coatings deposited have a low thickness. These oxide electronic conductor coatings, disposed in the volume of the electrode of the porous layer, give the electrode an excellent electronic conductivity, in particular when the porous layer is formed from poorly electronic conductive electrode active material. This layer of oxide electronic conductor material can improve the electrical conductivity of the electrode while limiting the dissolving of the electrode, and thus makes it possible to increase the power of the battery; which is all the more true since the coating layer of oxide electronic conductor material with zones of electrode active material P has a low thickness.

This is essentially the singular structure of the porous electrode produced according to the method according to the invention comprising zones of electrode active material P covered with a coating of the oxide electronic conductor material throughout the internal volume of the electrode as well as at the surface, which makes it possible to improve the final properties of the electrode, in particular to obtain thick electrodes without increasing the internal resistance of the electrode.

This coating of an oxide electronic conductor material throughout the internal volume of the electrode, coating the zones of electrode active material P, typically has a thickness less

than 10 nm, preferably less than 7 nm, more preferably less than 5 nm, still more preferably between 5 nm and 3 nm and still more preferably less than 3 nm. The coating of the oxide electronic conductor material throughout the internal volume of the electrode advantageously has an optimum thickness; this coating must be sufficiently thick to improve the electronic conduction, and sufficiently thin not to hinder the ionic conduction inside the electrode, and ultimately so as not to degrade the performance of the electrical energy storage or production device such as a battery. Furthermore, this coating gives the electrode a good electronic conduction due to the large specific surface area of the electrode.

10

Advantageously, said electronic conductor material can be an oxide electronic conductor material, preferably chosen from:

- tin oxide (SnO_2), zinc oxide doped with aluminium (ZnO:Al), preferably having a molar ratio Zn: Al between 1: 0.015 and 1: 0.05, indium oxide (In_2O_3), gallium oxide (Ga_2O_3), molybdenum oxide (MoO_3), strontium molybdenum oxide (SrMoO_3), a mixture of two of these oxides such as indium tin oxide corresponding to a mixture of indium oxide (In_2O_3) and tin oxide (SnO_2), a mixture of three of these oxides, a mixture of four of these oxides, a mixture of five of these oxides or a mixture of six of these oxides,
- doped oxides based on zinc oxide, the doping being preferably with gallium (Ga) and/or aluminium (Al) and/or boron (B) and/or beryllium (Be), and/or chromium (Cr) and/or cerium (Ce) and/or titanium (Ti) and/or indium (In) and/or cobalt (Co) and/or nickel (Ni) and/or copper (Cu) and/or manganese (Mn) and/or germanium (Ge) and/or molybdenum (Mo),
- doped oxides based on indium oxide, the doping being preferably with tin (Sn), and/or gallium (Ga) and/or chromium (Cr) and/or cerium (Ce) and/or titanium (Ti) and/or indium (In) and/or cobalt (Co) and/or nickel (Ni) and/or copper (Cu) and/or manganese (Mn) and/or germanium (Ge) and/or molybdenum (Mo),
- doped tin oxides, the doping being preferably with arsenic (As) and/or fluorine (F) and/or nitrogen (N) and/or niobium (Nb) and/or phosphorus (P) and/or antimony (Sb) and/or aluminium (Al) and/or titanium (Ti), and/or gallium (Ga) and/or chromium (Cr) and/or cerium (Ce) and/or indium (In) and/or cobalt (Co) and/or nickel (Ni) and/or copper (Cu) and/or manganese (Mn) and/or germanium (Ge) and/or molybdenum (Mo),
- doped oxides based on molybdenum oxide, the doping being preferably with lithium (Li) and/or sodium (Na) and/or potassium (K) and/or beryllium (Be) and/or magnesium (Mg) and/or calcium (Ca) and/or scandium (Sc) and/or titanium (Ti) and/or vanadium (V) and/or chromium (Cr) and/or manganese (Mn) and/or iron (Fe) and/or cobalt (Co) and/or nickel (Ni) and/or copper (Cu) and/or zinc (Zn) and/or gallium (Ga) and/or germanium (Ge) and/or

arsenic (As) and/or rubidium (Rb) and/or caesium (Cs) and/or yttrium (Y) and/or zirconium (Zr), and/or strontium (Sr) and/or niobium (Nb) and/or tritium (T) and/or rhenium and/or iridium (Ir) and/or platinum (Pt) and/or gold (Au) and/or mercury (Hg) and/or lead (Pb) and/or bismuth (Bi).

5

6. Consolidation of the porous layer comprising an electrode active material P and an oxide electronic conductor material, in order to obtain a porous, preferably mesoporous, electrode.

The porous layers or self-supporting porous plates can then be heat treated, preferably in an oxidising atmosphere, if necessary, in order to eliminate the organic constituents. The porous layers or self-supporting porous plates can then be consolidated. This consolidation can be carried out by pressing and/or heat treatment, i.e. by a heat treatment (heating), by a heat treatment preceded by a mechanical treatment, and optionally by a thermomechanical treatment, typically a thermocompression. In a very advantageous embodiment of the invention, this treatment leads to a partial coalescence, on the one hand, of the primary nanoparticles into aggregates or agglomerates, and, on the other hand, between neighbouring aggregates or agglomerates via the presence of the coating of an oxide electronic conductor material; 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 (restricted) neck. The lithium ions and electrons are mobile within these necks and can diffuse from one particle to another without encountering grain boundaries. The nanoparticles are welded together, in order to ensure the conduction of electrons from one to another. The neighbouring aggregates or agglomerates are welded together via the presence of the coating of an oxide electronic conductor, in order to ensure the conduction of electrons from one aggregate or agglomerate to another. The electronic conduction is carried out by two different means, in particular by the nanoparticles of electrode active material P (1) welded together, and by the neighbouring aggregates or agglomerates welded together via an oxide electronic conductor material (2); this is illustrated schematically in figure 1.

Thus, a rigid mesoporous film, without organic binder, is formed from primary nanoparticles of electrode active material P (1) and of the oxide electronic conductor material (2), forming a three-dimensional network with high ionic mobility and electronic conduction; this network includes interconnected pores, preferably mesopores. This porous, preferably mesoporous, layer thus obtained, is perfectly well adapted to the impregnation of the pores of the

electrode by an ionic conductor material, which enters into the depth of the open porous structure of the layer.

The temperature necessary in order to obtain the "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 repercussions on the porosity. It is thus possible to obtain an electrode with a desired porous or mesoporous ceramic structure with controlled porosity, while maintaining a perfectly homogeneous channel size. During this thermomechanical or heat treatment, the electrode layer will be freed of any organic constituent and residue (such as the liquid phase of the suspension of nanoparticles, binders and optionally surfactant products): it becomes an inorganic (ceramic) layer.

These porous electrodes or plates, centred in this way, have a thickness advantageously less than or equal to 5 mm, preferably between approximately 1 μm and approximately 500 μm . The thickness of the porous plate after sintering is advantageously between 2 μm and 400 μm , preferably between 2 μm and 300 μm , more preferably between 3 μm and 200 μm . According to the second embodiment and in order to obtain a porous electrode disposed on a substrate capable of acting as current collector, an electrically conductive sheet is also provided, covered on at least one of its faces, preferably on both its faces, by a thin layer of conductive adhesive (loaded with graphite), or a sol-gel deposit charged with conductive particles. Said thin layers preferably have a thickness less than 1 μm . This electrically conductive sheet can be a metallic strip or a sheet of graphite.

When said electrically conductive sheet is metallic, it is preferably a laminated sheet, i.e. obtained by lamination. The lamination can optionally be followed by a final annealing, which can be a (total or partial) softening annealing or for recrystallisation, according to metallurgy terminology. It is also possible to use a sheet obtained by electrolytic deposition, for example an electrodeposited copper sheet or an electrodeposited nickel sheet.

This electrically conductive sheet is then disposed on a plate or inserted between two previously obtained plates after consolidation (i.e. sintering). The assembly is then advantageously pressed so that said intermediate thin layer of conductive adhesive promotes the adhesion of the plate to the substrate and forms a plate/substrate or plate/substrate/plate assembly in order to obtain a rigid, one-piece subassembly.

One of the advantages of the second embodiment is that it makes it possible to use less expensive substrates, such as aluminium strips, copper or graphite strips. More particularly,

these strips cannot withstand the heat treatments for consolidating the deposited layers; the fact of having bonded them on the plates after their heat treatment also makes it possible to avoid their oxidation.

The plate/substrate or plate/substrate/plate subassemblies thus obtained, can be used in
5 the production of an electrochemical device, such as a battery.

Optionally, the porous electrode according to the invention, preferably the self-supporting porous plate, can be impregnated by an ionic conducting phase, i.e. a phase comprising at least one ionic conductor material, such as an ionic conductor polymer or an ionic liquid
10 polymer. This ionic conductor material can also have electronic conduction. The ionic conductor materials can be of different types. They can be liquid, in the form of gels, but also solid. The impregnation by solid ionic conductors is advantageously carried out through the use of ionic conductors in the molten state or dissolved in a solvent which will be subsequently evaporated. The ionic conductive phase can comprise or be an ionic
15 conductor polymer, preferably chosen from polyethylene oxide (PEO), polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(propylene carbonate) (PPC), poly(ethylene carbonate) (PEC), poly(vinyl carbonate) (PVC), polyvinylidene fluoride (PVDF), polypropylene glycol (PPG), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), polydimethylsiloxane (PDMS), poly(ϵ -caprolactone) (PCL) and poly(trimethylene
20 carbonate) (PTMC).

The presence of an ionic conductor polymer in the pores of the porous electrode, preferably in the pores of the self-supporting porous plate, gives it better mechanical rigidity. The use of a porous electrode according to the invention impregnated with an ionic conductor polymer within an energy storage or production device, such as battery, can increase its
25 service life.

Optionally, a layer can be deposited on top of the porous electrode according to the invention, which is electronically insulating and which has good ionic conductivity; its thickness is typically of order 0.5 nm to 20 nm, preferably less than 5 nm, and still more preferably less than 2 nm.

Said ionically conductive and electronically insulating layer can be inorganic or organic in nature. More particularly, the inorganic layers which can be used include, for example, an oxide, phosphate or borate conductor of lithium ions, and the organic layers that can be used include polymers (for example PEO optionally containing lithium salts, or a tetrafluoroethylene sulfonate copolymer such as the Nafion™, CAS no. 31175-20-9). This
35 ionically conductive and electronically insulating layer must be stable in contact with the

electrode on which it is deposited. The use of a borate conductor of lithium ions will be preferred on a cathode.

This ionically conducting and electronically insulating layer makes it possible to limit the dissolution of ions from the electrode and their migration towards the electrolyte, understanding that in electrodes made of LiMn_2O_4 , the manganese is at risk of dissolving in certain liquid electrolytes, in particular at high temperature.

When the electrode according to the invention is covered with an ionically conducting layer, it is the latter which mainly ensures the protective functions, as described above (in particular avoiding dissolving of the electrode).

To summarise, the presence of zones of electrode active material P, at least partially covered with a coating of oxide electronic conductor material, preferably covered with a coating of the oxide electronic conductor material throughout the internal volume of the electrode and at the surface of the porous electrode according to the invention, allows at least an increase in electronic conductivity and, depending on of the nature of the oxide electronic conductor material, can advantageously enable protection of the electrode against dissolving in the electrolyte at high temperature. Either these two effects are obtained with only the singular arrangement of the oxide electronic conductor material throughout the internal volume and at the surface of the electrode according to the invention, or this particular arrangement of the oxide electronic conductor material throughout the internal volume of the electrode according to the invention is not sufficient to obtain the two effects, in which case it is possible to deposit, on and inside the pores of the electrode according to the invention, for example, an ionically conductive and electronically insulating layer; in order to obtain additional protection at high temperature.

According to the first and second embodiment, a porous electrode according to the invention is obtained, disposed on a metal substrate acting as electronic current collector or situated on either side of a metal substrate acting as electronic current collector. The electrode/substrate/electrode subassemblies thus obtained, by the first or second embodiment, can be used in the production of an electrochemical device such as a battery, and in particular a microbattery. An assembly by thermal welding can also be carried out by stacking and thermopressing the assembly of the structure of the electrochemical device (such as a battery and in particular a microbattery); in this case, a multilayer stack is assembled comprising a first anode according to the invention, its metal substrate, a second anode according to the invention, a layer of the solid electrolyte or an electrolytic separator, a first cathode according to the invention, its metal substrate, a second cathode according to the invention, a new layer of solid electrolyte or a new electrolytic separator, and so on.

This electrode/substrate/electrode subassembly can be used to produce electrochemical devices such as batteries (and in particular microbatteries). Whatever the embodiment of the electrode/substrate/electrode subassembly, the electrolyte film or electrolytic separator is then deposited on the latter. Then, the necessary cuts are made in order to produce a battery with a plurality of elementary cells, then the subassemblies are stacked (typically "head to tail") and the thermocompression is carried out in order to weld together the anodes and cathodes of the solid electrolyte.

Alternatively, the cuts necessary to produce a battery with a plurality of elementary cells can be carried out before depositing an electrolyte film or an electrolytic separator, on each anode/substrate/anode and cathode/substrate/cathode subassembly. Then the anode/substrate/anode subassemblies and/or the cathode/substrate/cathode subassemblies are covered with an electrolyte film or an electrolytic separator, then the subassemblies are stacked and the thermocompression is carried out in order to weld together the anodes and cathodes at the electrolyte film or the electrolytic separator and, if necessary, the stack obtained is impregnated with an electrolyte, preferably a phase carrying lithium, sodium or potassium ions.

In the two alternatives which have just been presented, the welding by thermocompression can be carried out at a relatively low temperature, in particular when the electrodes according to the invention are impregnated by an ionic conductor material which can be an ionic conductor polymer or an ionic liquid polymer. For this reason, no oxidation of the metallic layers of the substrate is observed.

EXAMPLES

Example 1: Production of a LiMn_2O_4 -based mesoporous cathode according to the invention

An aqueous suspension of LiMn_2O_4 nanoparticles is prepared by hydrothermal synthesis according to the method described in the article by Liddle et al. entitled "*A new one pot hydrothermal synthesis and electrochemical characterisation of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinel structured compounds*", Energy & Environmental Science (2010) vol.3, page 1339-1346: 14.85 g of $\text{LiOH}\cdot\text{H}_2\text{O}$ were dissolved in 500 mL of water. To this solution was added 43.1g of KMnO_4 and this liquid phase was poured into an autoclave. Under stirring, 28 ml of isobutyraldehyde and water were added until a total volume of 3.54 L was obtained. The autoclave was then heated to 180°C and held at this temperature for 6 hours. After slow cooling, a black precipitate was obtained in suspension in the solvent. This precipitate was subjected to a succession of centrifugation steps - dispersed again in water, until an

aggregated suspension was obtained with a conductivity of approximately 300 $\mu\text{S}/\text{cm}$ and a zeta potential of -30 mV. The aggregates obtained were formed of aggregated primary particles of size from 10 to 20 nm. The aggregates obtained had a spherical shape and an average diameter of approximately 150 nm; they were characterised by x-ray diffraction and electron microscopy.

1 g of polyvinyl pyrrolidone (abbreviated as PVP) of molar mass 55,000 g/mol was added to 50 mL of distilled water at 40°C, then 3 g of tin acetate were added to this aqueous solution of PVP.

10 The LiMn_2O_4 suspension was reconcentrated by centrifugation and redispersion of the pellet in the volume of water necessary in order to obtain a 16% by weight paste. The volume of this aqueous solution of PVP and tin acetate corresponding to a ratio of 10% by mass of tin acetate relative to LiMn_2O_4 , as well as the necessary quantity of water, was then added to the suspension of LiMn_2O_4 of aggregates of nanoparticles in order to obtain a final
15 suspension of aggregates having a solids content of 10%.

The ink thus obtained was applied on a stainless steel (316L) strip of thickness 5 μm . The layer obtained was dried in a temperature-controlled oven. The layer obtained has a thickness of approximately 6 μm .

This layer was then heat-treated at 600°C for 5 hours in air, in order, on the one hand, to
20 carry out the transformation of the tin acetate, precursor of the oxide electronic conductor material, into SnO_2 , i.e. into oxide electronic conductor material, to remove the reaction by-products, and on the other hand, in order to weld together the primary nanoparticles and in order to weld together the neighbouring aggregates through the presence of the oxide electronic conductor material SnO_2 formed, in order to improve the adherence to the
25 substrate and to perfect the recrystallisation of the LiMn_2O_4 . The porous layer thus obtained has an open porosity of approximately 45% by volume with pores of a size between 10 nm and 20 nm.

Example 2: Production of a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based mesoporous anode according to the invention.

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A suspension of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles was prepared by glycothermal synthesis: 190 mL of 1,4-butanediol were poured into a beaker, and 4.25 g of lithium acetate were added under stirring. The solution was held without stirring until the acetate was completely dissolved. 16.9 g of titanium butoxide were then taken under an inert atmosphere and introduced into
35 the acetate solution. The solution was then stirred for several minutes before being transferred into an autoclave previously filled with an additional 60 mL of butanediol. The

autoclave was then closed and purged with nitrogen for at least 10 minutes. The autoclave was then heated to 300°C at a rate of 3°C/min and held at this temperature for 2 hours, under stirring. Finally it was allowed to cool, while always continuing to stir.

A white precipitate was obtained in suspension in the solvent. This precipitate was subjected to a succession of centrifugation steps - redispersion in ethanol in order to obtain a pure colloidal suspension pure, with a low ionic conductivity. It comprised aggregates of approximately 150 nm formed of primary particles of 10 nm. The zeta potential was of order -45 mV. The product was characterised by x-ray diffraction and electron microscopy.

1 g of polyvinyl pyrrolidone (abbreviated as PVP) of molecular mass 55,000 g/mol was added to 50 mL of ethanol at 40°C, then 3 g of tin acetate were added to this solution of PVP.

Then, to this suspension of aggregates of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles, was added the volume of this solution of PVP and tin acetate corresponding to a ratio of 10% by mass of tin acetate relative to $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The ethanol was evaporated until the suspension of aggregates had a solids content of 10%. The ink thus obtained was applied on a stainless steel (316L) strip of thickness 5 μm . The layer obtained was dried in a temperature- and humidity-controlled oven, in order to avoid the formation of cracks during drying. The deposition of ink and drying were then repeated in order to obtain a layer of approximately 4 μm thickness. This layer was then heat-treated at 600°C for 5 hours in air. This heat treatment enables the transformation of the tin acetate, precursor of the oxide electronic conductor material, into SnO_2 , i.e. into oxide electronic conductor material, to be carried out, to eliminate the reaction by-products, and thus form a porous layer comprising aggregates of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles covered with a homogeneous coating of SnO_2 , and to consolidate the layer, i.e to weld together the nanoparticle primaries and to weld together the neighbouring aggregates via the presence of the formed oxide electronic conductor material SnO_2 , to improve the adherence to the substrate of aggregates of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles covered with a coating of SnO_2 and to perfect the recrystallisation of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Example 3: Production of a battery using a porous cathode and a porous anode according to the invention

a. Production of a suspension of nanoparticles of Li_3PO_4

Two solutions were prepared. 11.44 g of CH_3COOLi , $2\text{H}_2\text{O}$ were dissolved in 112 ml of water, then 56 ml of water were added under vigorous stirring of the medium in order to obtain a solution A. 4.0584 g of H_3PO_4 were diluted in 105.6 ml of water, then 45.6 ml of

ethanol were adding to this solution in order to obtain a second solution, hereinafter called solution B.

Solution B was then added, under vigorous stirring, to solution A. The solution obtained, which was perfectly clear after the disappearance of the bubbles formed during mixing, was added to 1.2 litres of acetone under the action of an Ultraturrax™ homogeniser in order to homogenise the medium. A white precipitate in suspension in the liquid phase was immediately observed.

The reaction medium was homogenised for 5 minutes then held for 10 minutes under magnetic stirring. It was allowed to decant for 1 to 2 hours. The supernatant was discarded then the remaining suspension was centrifuged for 10 minutes at 6000 rpm. Then, 300 ml of water was added in order to return the precipitate to suspension (use of a sonotrode, magnetic stirring). Under vigorous stirring, 125 ml of a solution of sodium tripolyphosphate at 100g/l was added to the colloidal suspension thus obtained. The suspension then became more stable. The suspension was then sonicated using a sonotrode. The suspension was then centrifuged for 15 minutes at 8000 rpm. The pellet was then redispersed in 150 ml of water. Then, the suspension obtained was again centrifuged for 15 minutes at 8000 rpm and the pellets obtained were re-dispersed in 12 mL of water. Agglomerates of approximately 100 nm formed of primary particles of Li_3PO_4 of 10 nm were thus obtained in suspension in water.

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b. Production, on the previously formed anode and cathode layers, of a porous inorganic layer from the suspension of Li_3PO_4 nanoparticles previously described in part a).

Porous, thin layers of Li_3PO_4 were then deposited by coating on the surface of the previously formed anode and cathode, from the suspension of previously obtained Li_3PO_4 nanoparticles, in order to obtain a layer with a thickness of approximately 3 μm . This layer was then dried in air at 120°C in order to remove any trace of organic residues, and it was then calcined at 350°C for one hour in air.

c. Production of an electrochemical cell

After having deposited 3 μm of porous Li_3PO_4 on each of the previously formed electrodes (cf. examples 1 & 2), the two subsystems were stacked so that the films of Li_3PO_4 were in contact. This stack was then hot pressed under vacuum.

In order to do this, the stack was placed under a pressure of 1.5 MPa, then dried under vacuum for 30 minutes at 10^{-3} bars. The plates of the press were then heated to 450°C at a rate of 4°C/second. At 450 °C, the stack was then thermocompressed under a pressure of 45 MPa for 1 minute, then the system was cooled to ambient temperature.

Once the assembly was carried out, a rigid multilayer system formed of one or more assembled battery cells was obtained.

This assembly was then impregnated in an electrolytic solution comprising 0.7 M LiTFSI in PYR14TFSI. The electrolyte instantly entered the pores by capillary action. The system was
5 held immersed for 1 minute, then the surface of the cell stack was dried by an N₂ blade.

CLAIMS

1. A method for producing a porous electrode, in particular for electrical energy storage or production devices, said electrode being a porous layer comprising at least one electrode active material P and an oxide electronic conductor material, said electrode being free of binder, having a porosity between 25% and 60% by volume, preferably between 25% and 50%, and pores of average diameter less than 100 nm, said production method being characterised in that it comprises:
 - (a) providing a substrate, at least one oxide electronic conductor material precursor, and a colloidal suspension or a paste comprising aggregates or agglomerates of primary nanoparticles of at least one electrode active material P, of primary median diameter D_{50} between 2 nm and 400 nm, preferably between 2 nm and 100 nm, and more preferably between 2 nm and 60 nm, said aggregates or agglomerates having a median diameter D_{50} between 50 nm and 900 nm, and preferably between 100 nm and 800 nm, understanding that said substrate can be a substrate capable of acting as electric current collector, or being an intermediate substrate,
 - (b) mixing said one or more precursors of an oxide electronic conductor material and said colloidal suspension or said paste comprising aggregates or agglomerates of primary nanoparticles of at least one electrode active material P provided in step (a), so as to form a mixture,
 - (c) forming a layer from the mixture obtained at the end of step (b), by a method selected from the group consisting of: electrophoresis, an additive manufacturing method, extrusion, a printing method, preferably inkjet printing or flexographic printing, a coating method, preferably doctor blade coating, roll coating, curtain coating, dip coating, or slot-die coating,
 - (d) drying said layer obtained in step (c) so as to obtain a dried layer, where appropriate said dried layer is separated from its intermediate substrate after drying step (d),
 - (e) transforming the one or more oxide electronic conductor material precursors into oxide electronic conductor material, so that said dried layer comprises said oxide electronic conductor material,
 - (f) consolidating said layer, by heat and/or mechanical treatment, preferably by sintering, in order to obtain a porous, preferably mesoporous electrode, it being understood that steps (e) and (f) can be carried out during a same heat treatment.

2. The method for producing a porous electrode according to claim 1, characterised in that step (b) is performed by placing the colloidal suspension or the paste provided in step (a), comprising aggregates or agglomerates of primary nanoparticles of at least one electrode active material P, in contact with a liquid phase containing at least one precursor of said oxide electronic conductor material, and in that said transformation of the one or more oxide electronic conductor material precursors into an oxide electronic conductor material during step (e) is carried out by heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere.
- 10 3. The method for producing a porous electrode according to claim 1 or 2, characterised in that after step (f), the pores of said porous electrode are impregnated by an electrolyte, preferably by a phase carrying lithium ions, sodium ions or potassium ions selected from the group consisting of:
- an electrolyte composed of at least one aprotic solvent and of at least one lithium, sodium or potassium salt;
 - an electrolyte composed of at least one ionic liquid and of at least lithium, sodium or potassium salt;
 - a mixture of at least one aprotic solvent and of at least one ionic liquid and of at least one lithium, sodium or potassium salt;
 - 20 - an ionic liquid polymer;
 - a polymer made ionic conductor by the addition of at least one lithium, sodium or potassium salt; and
 - a polymer made ionic conductor by the addition of a liquid electrolyte, either in the polymer phase, or in the porous structure of the porous electrode,
 - 25 or by an ionic conductor polymer, preferably chosen from polyethylene oxide (PEO), polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(propylene carbonate) (PPC), poly(ethylene carbonate) (PEC), poly(vinyl carbonate) (PVC), polyvinylidene fluoride (PVDF), polypropylene glycol (PPG), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), polydimethylsiloxane (PDMS), poly(ϵ -caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC).
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4. The method for producing a porous electrode according to any one of claims 1 to 3, characterised in that said one or more oxide electronic conductor material precursors are chosen from organic salts containing one or more metallic elements capable, after heat treatment such as calcination, of forming an oxide electronic conductor, and in that said transformation into electronic conductor material is a heat treatment such as
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calcination, preferably carried out in air or in an oxidising atmosphere, these organic salts being, preferably, chosen from

- an alcoholate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor,
- a nitrate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor,
- an oxalate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor, and
- an acetate of at least one metallic element capable, after heat treatment such as calcination, preferably carried out in air or in an oxidising atmosphere, of forming an oxide electronic conductor,
- and/or in that, preferably, the metallic element is chosen from tin, zinc, indium, gallium, molybdenum or a mixture of two or three or four or five of these elements.

5. The method for producing a porous electrode according to any one of claims 1 to 4, characterised in that said oxide electronic conductor material is chosen from:
- tin oxide (SnO_2), zinc oxide doped with aluminium (ZnO:Al), preferably having a molar ratio Zn: Al between 1: 0.015 and 1: 0.05, indium oxide (In_2O_3), gallium oxide (Ga_2O_3), molybdenum oxide (MoO_3), strontium molybdenum oxide (SrMoO_3), a mixture of two of these oxides such as indium tin oxide corresponding to a mixture of indium oxide (In_2O_3) and tin oxide (SnO_2), a mixture of three of these oxides, a mixture of four of these oxides, a mixture of five of these oxides or a mixture of six of these oxides,
 - doped oxides based on zinc oxide, the doping being preferably with gallium (Ga) and/or aluminium (Al) and/or boron (B) and/or beryllium (Be), and/or chromium (Cr) and/or cerium (Ce) and/or titanium (Ti) and/or indium (In) and/or cobalt (Co) and/or nickel (Ni) and/or copper (Cu) and/or manganese (Mn) and/or germanium (Ge) and/or molybdenum (Mo),
 - doped oxides based on indium oxide, the doping being preferably with tin (Sn), and/or gallium (Ga) and/or chromium (Cr) and/or cerium (Ce) and/or titanium (Ti) and/or indium (In) and/or cobalt (Co) and/or nickel (Ni) and/or copper (Cu) and/or manganese (Mn) and/or germanium (Ge) and/or molybdenum (Mo),
 - doped tin oxides, the doping being preferably with arsenic (As) and/or fluorine (F) and/or nitrogen (N) and/or niobium (Nb) and/or phosphorus (P) and/or antimony (Sb) and/or

aluminium (Al) and/or titanium (Ti), and/or gallium (Ga) and/or chromium (Cr) and/or cerium (Ce) and/or indium (In) and/or cobalt (Co) and/or nickel (Ni) and/or copper (Cu) and/or manganese (Mn) and/or germanium (Ge) and/or molybdenum (Mo),

- doped oxides based on molybdenum oxide, the doping being preferably with lithium (Li) and/or sodium (Na) and/or potassium (K) and/or beryllium (Be) and/or magnesium (Mg) and/or calcium (Ca) and/or scandium (Sc) and/or titanium (Ti) and/or vanadium (V) and/or chromium (Cr) and/or manganese (Mn) and/or iron (Fe) and/or cobalt (Co) and/or nickel (Ni) and/or copper (Cu) and/or zinc (Zn) and/or gallium (Ga) and/or germanium (Ge) and/or arsenic (As) and/or rubidium (Rb) and/or caesium (Cs) and/or yttrium (Y) and/or zirconium (Zr), and/or strontium (Sr) and/or niobium (Nb) and/or tritium (T) and/or rhenium and/or iridium (Ir) and/or platinum (Pt) and /or gold (Au) and/or mercury (Hg) and/or lead (Pb) and/or bismuth (Bi).

6. The method for producing a porous electrode according to any one of claims 1 to 5, characterised in that said porous electrode obtained at the end of step (f) has a specific surface area between $10 \text{ m}^2/\text{g}$ and $500 \text{ m}^2/\text{g}$ and/or a thickness between $2 \text{ }\mu\text{m}$ and $400 \text{ }\mu\text{m}$, preferably between $2 \text{ }\mu\text{m}$ and $300 \text{ }\mu\text{m}$, more preferably between $3 \text{ }\mu\text{m}$ and $200 \text{ }\mu\text{m}$.

7. The method for producing a porous electrode according to any one of claims 1 to 5, characterised in that said porous electrode obtained at the end of step (f) has a specific surface area between $10 \text{ m}^2/\text{g}$ and $500 \text{ m}^2/\text{g}$; and/or a thickness between $2 \text{ }\mu\text{m}$ and $20 \text{ }\mu\text{m}$ when the substrate is a substrate capable of acting as electric current collector, and/or a thickness between $25 \text{ }\mu\text{m}$ and $500 \text{ }\mu\text{m}$, preferably between $50 \text{ }\mu\text{m}$ and $400 \text{ }\mu\text{m}$, when the substrate is an intermediate substrate.

8. The method for producing a porous electrode according to any one of claims 1 to 5, characterised in that when said substrate is an intermediate substrate, said layer is separated from said intermediate substrate in step (d) after drying of said layer, in order to form a porous plate.

9. The method for producing a porous electrode according to any one of claims 1 to 8, characterised in that said colloidal suspension or paste provided in step (a) comprises organic additives, such as ligands, stabilisers, binders or residual organic solvents, and a heat treatment, preferably in an oxidising atmosphere, of said dried layer obtained at the end of step d) according to any one of claims 1 to 7, or of said porous plate according to

claim 8, is performed, it being understood that this heat treatment and steps (e) and/or (f) can be carried out during a same heat treatment step.

10. The method for producing a porous electrode according to any one of claims 1 to 9, in which said electrode active material P is selected from the group (A) consisting of:
- 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 $x+y+z=10$;
 - $\text{Li}_x\text{M}_y\text{O}_2$ where $0.6 \leq y \leq 0.85$; $0 \leq x+y \leq 2$; and M is chosen from Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Sn, and Sb or a mixture of these elements; $\text{Li}_{1.20}\text{Nb}_{0.20}\text{Mn}_{0.60}\text{O}_2$;
 - $\text{Li}_{1+x}\text{Nb}_y\text{Me}_z\text{A}_p\text{O}_2$ where Me is at least one transition metal chosen 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, 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 $0 \leq p \leq 0.2$;
 - $\text{Li}_x\text{Nb}_{y-a}\text{NaM}_{z-b}\text{P}_c\text{O}_{2-c}\text{F}_c$ 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 chosen from the group consisting of Ti, Ta, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Zr, Y, Mo, Ru, Rh, Ce and Sb;
 - $\text{Li}_{1.25}\text{Nb}_{0.25}\text{Mn}_{0.50}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.40}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Fe}_{0.40}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.43}\text{Ni}_{0.27}\text{O}_2$; $\text{Li}_{1.3}\text{Nb}_{0.43}\text{Co}_{0.27}\text{O}_2$; $\text{Li}_{1.4}\text{Nb}_{0.2}\text{Mn}_{0.53}\text{O}_2$;
 - $\text{Li}_x\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_y$ where $0.00 \leq x \leq 1.52$; $1.07 \leq y < 2.4$; $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$;
 - $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ 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 $0 \leq z$;
 - 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 M = Fe, Co, Ni or a mixture of these different elements, LiMPO_4F with M = V, Fe, T or a mixture of these different elements; phosphates of formula $\text{LiMM}'\text{PO}_4$, with M and M' ($M \neq M'$) selected from Fe, Mn, Ni, Co, V such as $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ and where $0 < x < 1$;
 - $\text{Fe}_{0.9}\text{Co}_{0.1}\text{OF}$; FeF_3 ; LiMSO_4F with M = Fe, Co, Ni, Mn, Zn, Mg;
 - 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 , $\text{Li}_x\text{V}_2\text{O}_5$ 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 $\text{Li}_x\text{TiO}_y\text{S}_z$ 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 $0 < x \leq 1$;
- or in the group (B) consisting of:
- transition metal oxides:

- $\text{Na}_x\text{MO}_{2+z}$ with M chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;
- 5 ○ $\text{Na}_x\text{M}_{u/2}\text{M}'_{v/2}\text{O}_{2+z}$ with $u + v = 2$ and M, M' chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;
- $\text{Na}_x\text{M}_{u/3}\text{M}'_{v/3}\text{M}''_{w/3}\text{O}_{2+z}$ with $u + v + w = 3$ and M, M', M'' chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;
- 10 ○ $\text{Na}_x\text{Mn}_y\text{Ni}_z\text{Fe}_{0.1}\text{Mg}_{0.1}\text{O}_2$ with $0.67 \leq x \leq 1.0$; $0.5 \leq y \leq 0.7$ and $0.1 \leq z \leq 0.3$;
- Prussian blue and/or Prussian blue analogues, known by the abbreviation PBA:
 - 15 ○ $\text{Na}_x\text{M}^1[\text{M}^{2'}(\text{CN})_6]_y \cdot n\text{H}_2\text{O}$, M^1 being a transition metal or a transition metal alloy, $\text{M}^{2'}$ being a transition metal, the transition metal and the transition metal alloy being chosen from the Fe, Ni, Co and Mn, with $0 \leq x \leq 2$; $y \leq 1$ and $0 \leq n \leq 12$;
- polyanionic compounds:
 - 20 ○ $\text{Na}_x\text{M}_2(\text{XO}_4)_3$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$, such as $\text{Na}_3\text{V}_2(\text{PO}_4)_3$;
 - $\text{Na}_x\text{M}_3(\text{XO}_4)_2(\text{X}_2\text{O}_7)$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;
 - $\text{Na}_x\text{M}(\text{X}_2\text{O}_7)$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;
 - 25 ○ $\text{Na}_x\text{M}_2(\text{XO}_4)_2\text{F}_3$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;
 - $\text{Na}_x\text{M}_2(\text{XO}_4)_2\text{F}_{3-y}\text{O}_y$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $0.07 \leq y \leq 0.12$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;
 - $\text{Na}_x\text{M}_2\text{O}_2(\text{XO}_4)_2\text{F}$ with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;
 - 30 ○ Na_xMXO_4 with $0 < x \leq 4$, $\text{M} = \text{V, Fe, Cr, Mn, Co, Ni or Sc}$ and $\text{X} = \text{P, S, As, Si, Mo or W}$;

or in the group (C) consisting of:

- transition metal oxides:

- K_xMO_{2+z} with M chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;
- 5 ○ $K_xM_{u/2}M'_{v/2}O_{2+z}$ with $u + v = 2$ and M, M' chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;
- $K_xM_{u/3}M'_{v/3}M''_{w/3}O_{2+z}$ with $u + v + w = 3$ and M, M', M'' chosen from Mg, Ca, Li, Mn, Ni, Co, Cr, Sc, Te with $z \leq 0.3$ and $0 < x \leq 1$, preferably $0 < x < 0.44$ or $0.44 \leq x \leq 0.67$ or $0.67 < x \leq 1$;
- 10 ○ $K_xMn_yNi_zFe_{0.1}Mg_{0.1}O_2$ with $0.67 \leq x \leq 1.0$; $0.5 \leq y \leq 0.7$ and $0.1 \leq z \leq 0.3$;
- Prussian blue and/or Prussian blue analogues, known by the abbreviation PBA:
 - $K_xM^1[M^{2'}(CN)_6]_y \cdot nH_2O$, M^1 being a transition metal or a transition metal alloy, $M^{2'}$ being a transition metal, the transition metal and the transition metal alloy being chosen from the Fe, Ni, Co and Mn, with $0 \leq x \leq 2$; $y \leq 1$ and $0 \leq n \leq 12$;
- polyanionic compounds:
 - $K_xM_2(XO_4)_3$ with $0 < x \leq 4$, M = V, Fe, Cr, Mn, Co, Ni or Sc and X = P, S, As, Si, Mo or W, such as $Na_3V_2(PO_4)_3$;
 - 20 ○ $K_xM_3(XO_4)_2(X_2O_7)$ with $0 < x \leq 4$, M = V, Fe, Cr, Mn, Co, Ni or Sc and X = P, S, As, Si, Mo or W;
 - $K_xM(X_2O_7)$ with $0 < x \leq 4$, M = V, Fe, Cr, Mn, Co, Ni or Sc and X = P, S, As, Si, Mo or W;
 - 25 ○ $K_xM_2(XO_4)_2F_3$ with $0 < x \leq 4$, M = V, Fe, Cr, Mn, Co, Ni or Sc and X = P, S, As, Si, Mo or W;
 - $K_xM_2(XO_4)_2F_{3-y}O_y$ with $0 < x \leq 4$, M = V, Fe, Cr, Mn, Co, Ni or Sc and $0.07 \leq y \leq 0.12$ and X = P, S, As, Si, Mo or W;
 - $K_xM_2O_2(XO_4)_2F$ with $0 < x \leq 4$, M = V, Fe, Cr, Mn, Co, Ni or Sc and X = P, S, As, Si, Mo or W;
 - 30 ○ K_xMXO_4 with $0 < x \leq 4$, M = V, Fe, Cr, Mn, Co, Ni or Sc and X = P, S, As, Si, Mo or W.

11. The method for producing a porous electrode according to any one of claims 1 to 9, in which said electrode active material P is selected from the group (D) consisting of:

- $Li_4Ti_5O_{12}$, $Li_4Ti_{5-x}M_xO_{12}$ with M = V, Zr, Hf, Nb, Ta and $0 \leq x \leq 0.25$;

- niobium oxides and mixed oxides of niobium with titanium, germanium, cerium or tungsten, and preferably in the group consisting of:
 - $\text{Nb}_2\text{O}_{5\pm\delta}$, $\text{Nb}_{12}\text{WO}_{33\pm\delta}$, $\text{Nb}_{14}\text{W}_3\text{O}_{44\pm\delta}$, $\text{Nb}_{18}\text{W}_{16}\text{O}_{93\pm\delta}$, $\text{Nb}_{16}\text{W}_5\text{O}_{55\pm\delta}$ with $0 \leq \delta \leq 2$, LiNbO_3 ,
 - 5 ➤ $\text{TiNb}_2\text{O}_{7\pm\delta}$, $\text{Li}_w\text{TiNb}_2\text{O}_7$ 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 chosen in the group consisting 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 being able to be identical or different from one another, and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $0 \leq \delta \leq 0.3$;
 - 10 ➤ $\text{La}_x\text{Ti}_{1-2x}\text{Nb}_{2+x}\text{O}_7$ where $0 < x < 0.5$;
 - $\text{M}_x\text{Ti}_{1-2x}\text{Nb}_{2+x}\text{O}_{7\pm\delta}$ wherein M is an element for which the oxidation value is +III, more particularly M is at least one of the elements chosen in the group consisting of Fe, Ga, Mo, Al, B, and where $0 < x \leq 0.20$ and $-0.3 \leq \delta \leq 0.3$; $\text{Ga}_{0.10}\text{Ti}_{0.80}\text{Nb}_{2.10}\text{O}_7$; $\text{Fe}_{0.10}\text{Ti}_{0.80}\text{Nb}_{2.10}\text{O}_7$;
 - 15 ➤ $\text{M}_x\text{Ti}_{2-2x}\text{Nb}_{10+x}\text{O}_{29\pm\delta}$ wherein M is an element for which the oxidation value is +III, more particularly M is at least one of the elements chosen in the group consisting of Fe, Ga, Mo, Al, B, and where $0 < x \leq 0.40$ and $-0.3 \leq \delta \leq 0.3$;
 - 20 ➤ $\text{Ti}_{1-x}\text{M}^1_x\text{Nb}_{2-y}\text{M}^2_y\text{O}_{7-z}\text{M}^3_z$ 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
 - M^1 and M^2 are each at least one element chosen in the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs and Sn,
 - M^1 and M^2 being able to be identical or different from one another,
 - 25 - M^3 is at least one halogen,
 - and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
 - $\text{TiNb}_2\text{O}_{7-z}\text{M}^3_z$ or $\text{Li}_w\text{TiNb}_2\text{O}_{7-z}\text{M}^3_z$ wherein M^3 is at least one halogen, preferably chosen from F, Cl, Br, I or a mixture of these, and $0 \leq z \leq 0.3$ and $0 \leq w \leq 5$;
 - 30 ➤ $\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$, $\text{Li}_w\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$, $\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$, $\text{Li}_w\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7\pm z}$ wherein
 - M^1 is at least one element chosen in the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs and Sn;
 - 35 - $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;

- $\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$, $\text{Li}_w\text{Ti}_{1-x}\text{Ge}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$, $\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$, $\text{Li}_w\text{Ti}_{1-x}\text{Ce}_x\text{Nb}_{2-y}\text{M}^1_y\text{O}_{7-z}\text{M}^2_z$, wherein
- M^1 and M^2 are each at least one element chosen in the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs, Ce and Sn,
 - M^1 and M^2 being able to be identical or different from one another,
 - and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
- TiO_2 ; TiO_xN_y with $x < 2$ and $0 < y < 0.2$;
 - LiSiTON, the oxynitrides based on tin and silicon, and more particularly the formulation $\text{SiSn}_{0.87}\text{O}_{1.20}\text{N}_{1.72}$ and their lithiated forms;
 - nitrides and oxynitrides of type MO_xN_y , where M is at least one element chosen from Ge, Si, Sn, Zn, Co, Ni, Cu, Fe or a mixture of one or more of these elements, and where $x \geq 0$ and $y \geq 0.3$;
 - $\text{Li}_{3-x}\text{M}_x\text{N}$ with M is at least one element chosen from Cu, Ni, Co or a mixture of one or more of these elements and $0 \leq x \leq 1$;
 - $\text{Li}_{3-x}\text{M}_x\text{N}$ with M being cobalt (Co) and $0 \leq x \leq 0.5$; $\text{Li}_{3-x}\text{M}_x\text{N}$ with M being nickel (Ni) and $0 \leq x \leq 0.6$; $\text{Li}_{3-x}\text{M}_x\text{N}$ with M being copper (Cu) and $0 \leq x \leq 0.3$;
 - lithiated iron phosphate, of typical formula LiFePO_4 ;
 - mixed oxynitrides of silicon and tin, of typical formula $\text{Si}_a\text{Sn}_b\text{O}_y\text{N}_z$ with $a > 0$, $b > 0$, $a+b \leq 2$, $0 < y \leq 4$, $0 < z \leq 3$, also called SiTON, and in particular $\text{SiSn}_{0.87}\text{O}_{1.2}\text{N}_{1.72}$; as well as oxynitride carbides of typical formula $\text{Si}_a\text{Sn}_b\text{C}_c\text{O}_y\text{N}_z$ with $a > 0$, $b > 0$, $a+b \leq 2$, $0 < c < 10$, $0 < y < 24$, $0 < z < 17$;
 - nitrides of type Si_xN_y , in particular with $x=3$ and $y=4$; Sn_xN_y , in particular with $x=3$ and $y=4$, Zn_xN_y , in particular with $x=3$ and $y=2$; $\text{Li}_{3-x}\text{M}_x\text{N}$ with $0 \leq x \leq 0.5$ for $\text{M}=\text{Co}$, $0 \leq x \leq 0.6$ for $\text{M}=\text{Ni}$, $0 \leq x \leq 0.3$ for $\text{M}=\text{Cu}$; $\text{Si}_{3-x}\text{M}_x\text{N}_4$ with $\text{M}=\text{Co}$ or Fe and $0 \leq x \leq 3$.
 - oxides SnO_2 , SnO , Li_2SnO_3 , SnSiO_3 , Li_xSiO_y with $x \geq 0$ and $2 > y > 0$, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiNb_2O_7 , Co_3O_4 , $\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ and TiO_2 ,
 - Si, Sn, SiO_2 , SnO_2 , SiN, SnN and the mixtures thereof,
 - composite oxides TiNb_2O_7 comprising between 0% and 10% by mass of carbon, the carbon preferably being chosen from graphene and carbon nanotubes.
- or in the group (E) consisting of:
- alloys based on Si, Ge, Sn, Sb, Bi or P and the alloys of these various compounds
 - MXenes. MXenes are a class of two-dimensional materials with stoichiometry of type $\text{M}_{n+1}\text{X}_n\text{T}_x$ with M a transition metal, preferably chosen from Sc, Ti, V, Cr,

Y, Zr, Nb, Mo, Hf, Ta, W and X is chosen from C and/or N and T a surface termination chosen from F, Cl, I, Br, O, S, Se, Te, OH, NH₂, $1 \leq n \leq 4$

- conversion anode materials such as

- oxides of type G₂Ti₃O₇, G₄Ti₅O₁₂, GTi₂(PO₄)₃, G being Na or K
- oxides, sulfides, selenides and phosphides of the following elements and their alloys: Si, Ge, Sn, Sb, Bi.

12. A porous electrode that can be obtained by the method according to any one of claims 1 to 11.

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13. A method for producing an electrical energy storage or production device, using the production method of a porous electrode according to one of claims 1 to 11, or using a porous electrode according to claim 12.

14. The method according to claim 13, characterised in that said electrical energy storage or production device is selected from the group consisting of: capacitors, supercapacitors, hybrid supercapacitors, such as lithium-ion hybrid supercapacitors, sodium-ion hybrid supercapacitors, potassium-ion hybrid supercapacitors, photovoltaic cells, photochemical cells and batteries such as lithium-ion batteries, sodium-ion batteries and potassium-ion batteries.

15. The method according to claim 14, wherein said device is a lithium-ion battery, and the method for producing a porous electrode according to claim 10 is implemented in order to produce a cathode with the electrode active material P chosen in group (A), or the method according to claim 11 is implemented in order to produce an anode with the electrode active material P chosen in group (D).

16. The method according to claim 14, wherein said device is a sodium-ion battery and the method for producing a porous electrode according to claim 10 is implemented in order to produce a cathode with the electrode active material P chosen in group (B), or the method according to claim 11 is implemented in order to produce an anode with the electrode active material P chosen in group (E).

17. The method according to claim 14, wherein said device is a potassium-ion battery, and method for producing a porous electrode according to claim 10 is implemented in order to produce a cathode with the electrode active material P chosen in group (C), or the method

according to claim 11 is implemented in order to produce an anode with the electrode active material P chosen in group (E).

18. The method according to any one of claims 13 to 17, wherein said device is a
 5 lithium-ion, sodium-ion or potassium-ion battery and said porous electrode is impregnated by an electrolyte, preferably by a phase carrying lithium ions, sodium ions or potassium ions selected from the group consisting of:
- an electrolyte composed of at least one aprotic solvent and at least one lithium, sodium or potassium salt;
 - 10 - an electrolyte composed of at least one ionic liquid and at least lithium, sodium or potassium salt;
 - a mixture of at least one aprotic solvent and at least one ionic liquid and at least one lithium, sodium or potassium salt;
 - an ionic liquid polymer;
 - 15 - a polymer made ionic conductor by the addition of at least one lithium, sodium or potassium salt; and
 - a polymer made ionic conductor by the addition of a liquid electrolyte, either in the polymer phase, or in the porous structure,
- or by an ionic conductor polymer, preferably chosen from polyethylene oxide (PEO),
 20 polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(propylene carbonate) (PPC), poly(ethylene carbonate) (PEC), poly(vinyl carbonate) (PVC), polyvinylidene fluoride (PVDF), polypropylene glycol (PPG), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), polydimethylsiloxane (PDMS), poly(ϵ -caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC).

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19. An electrical energy storage or production device that can be obtained by the method according to any one of claims 13 to 18.

20. An electrical energy storage or production device according to claim 19,
 30 characterised in that it is a capacitor, a supercapacitor, a hybrid supercapacitor such as lithium-ion hybrid supercapacitor, a sodium-ion hybrid supercapacitor, a potassium-ion hybrid supercapacitor, a photovoltaic cell, a photochemical cell, or a battery such as a lithium-ion battery, a sodium-ion battery or a potassium-ion battery.