CLAIMS

1. Method for manufacturing a porous anode for a battery comprising an anode, a separator and a cathode, said anode comprising a porous layer having a porosity between 25% and 50% by volume, preferably about 35% by volume, and pores with an average diameter of less than 50 nm, said manufacturing method being characterised in that:

(a) a substrate and a colloidal suspension or a paste composed of monodisperse primary nanoparticles, in the form of agglomerates or dispersed, is provided of at least one active material of anode A, with an average primary diameter D_{50} of between 2 nm and 100 nm, and preferably of between 2 nm and 60 nm,

it being understood that said colloidal suspension or said paste also comprises a liquid constituent,

it being understood that said active material of anode A is selected from the group formed by:

- $TiNb_2O_{7-z}M^3_z$, $Li_wTiNb_2O_{7-z}M^3_z$ wherein M^3 is at least one halogen, preferably selected from F, Cl, Br, I or a mixture thereof, and $0 \leq w \leq 5$ and $0 < z \leq 0.3$;
- $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}$, $Ti_{1-x}La_xNb_{2-y}M^1_yO_{7-z}$, $Li_wTi_{1-x}La_xNb_{2-y}M^1_yO_{7-z}$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}$ wherein
  - M^1 is at least one element selected from the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs, Ce and Sn,
  - and wherein $0 \leq w \leq 5$ and $0 < x < 1$ and $0 \leq y < 2$ and $z < 1$, preferably wherein $0 \leq w \leq 5$ and $0 < x < 1$ and $0 \leq y < 2$ and $z < 0.3$;
- $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}La_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}La_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}Cu_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Cu_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$ wherein
  - M^1 and M^2 are at least one element selected from the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs and Sn ;
  - $0 \leq w \leq 5$ and $0 < x < 1$ and $0 \leq y < 2$ and $z \leq 0.3$;

(b) depositing on at least one face of said substrate a layer from said colloidal suspension or paste provided in step (a), by a method selected from the group formed by: electrophoresis, extrusion, a printing method and preferably inkjet printing or flexographic printing, a coating method, preferably by doctor blade, roll coating, curtain coating, dip coating or through a slot die;

(c) drying said layer obtained in step (b) and consolidating it by pressing and/or heating to obtain said porous layer of the anode.

2. Method according to claim 1, characterised in that the method is continued with step (d):

(d) depositing on and within the pores of said porous layer, a coating of an electronically conductive material, which is preferably selected from carbon or an electronically conductive oxide material, and where said electronically conductive oxide material is preferably selected from:

- tin oxide (SnO_2), zinc oxide (ZnO), indium oxide (In_2O_3), gallium oxide (Ga_2O_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 or a mixture of four 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),
- 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),
- 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).

3. Method according to claim 2, characterised in that the deposit of said coating of electronically conductive material is performed by atomic layer deposition ALD or by immersion in a liquid phase comprising a precursor of said electronically conductive material, followed by the transformation of said precursor into electronically conductive material.

4. Method according to claim 3, characterised in that said precursor is a carbon-rich compound, such as a carbohydrate, and in that said transformation into electronically conductive material is by pyrolysis, preferably in an inert atmosphere, or in that said

precursor is selected from organic salts containing one or more metal elements capable, after heat treatment such as calcination, of forming an electronically conductive oxide, and in that said transformation into electronically conductive material is a heat treatment such as calcination, preferably performed in air or in an oxidising atmosphere.

5. Method according to claim 4, characterised in that the organic salts are preferably selected from a group formed by an alcoholate, an oxalate and an acetate of at least one metal element capable, after heat treatment such as calcination preferably performed in air or in an oxidising atmosphere, of forming an electronically conductive oxide, , and/or in that the metal element is selected from tin, zinc, indium, gallium or a mixture of two or three or four of these elements.

6. Method according to any of claims 1 to 5, characterised in that said primary nanoparticles are in the form of aggregates or agglomerates, said aggregates or agglomerates having an average diameter D_{50} between 50 nm and 300 nm, and preferably between 100 nm and 200 nm.

7. Method according to any of claims 1 to 6, characterised in that said porous layer resulting from step (c) has a specific surface area of between 10 m^2/g and 500 m^2/g.

8. Method according to any of claims 1 to 7, wherein said layer obtained in step (c) has a thickness between 1 µm and 150 µm.

9. Method according to any of claims 1 to 8, characterised in that said substrate is an intermediate substrate, of which said layer is separated in step (c) after drying to form a porous anode plate.

10. Porous anode for a lithium-ion battery, comprising a porous layer with a porosity between 25% and 50% by volume, preferably between 28% and 43% by volume, and even more preferably between 30% and 40% by volume,
characterised in that said porous layer comprises:

- pores with an average diameter of less than 50 nm,
- a porous network of a material A comprising on and within the pores forming said porous network a coating of an electronically conductive material,

and characterised in that said material A is selected from the group formed by:

- $TiNb_2O_{7-z}M^3_z$, $Li_wTiNb_2O_{7-z}M^3_z$ wherein M^3 is at least one halogen, preferably selected from F, Cl, Br, I or a mixture thereof, and $0 < z \leq 0.3$,
- $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}$ wherein
  - M^1 is at least one element selected from the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs, Ce and Sn,
  - and wherein $0 \leq w \leq 5$ and $0 < x < 1$ and $0 \leq y < 2$ and $z < 1$, preferably wherein $0 \leq w \leq 5$ and $0 < x < 1$ and $0 \leq y < 2$ and $z < 0.3$;
- $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}La_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}La_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}Cu_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Cu_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$ wherein
  - M^1 and M^2 are at least one element selected from the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs and Sn;
  - $0 \leq w \leq 5$ and $0 < x < 1$ and $0 \leq y < 2$ and $z \leq 0.3$;

said anode being able to be obtained by the method according to any of claims 1 to 9.

11. Anode according to claim 10, characterised in that the electronically conductive material is selected from carbon, electronically conductive oxide materials, preferably selected from:

- tin oxide (SnO_2), zinc oxide (ZnO), indium oxide (In_2O_3), gallium oxide (Ga_2O_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 or a mixture of four 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),
- doped oxides based on indium oxide, the doping being preferably 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),
- 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).

12. Method for manufacturing a battery, preferably a lithium-ion battery, using the method for manufacturing a porous anode according to any of claims 1 to 9, or using a porous anode according to claim 10.

13. Method for manufacturing a battery, comprising at least one porous anode according to claim 10 or 11, at least one separator and at least one porous cathode, characterised in that:

(a) a first substrate, second substrate are provided and

- a first colloidal suspension or a paste comprising aggregates or agglomerates of monodisperse primary nanoparticles of at least one active material of anode A is provided, with an average primary diameter D_{50} between 2 and 100 nm, preferably between 2 and 60 nm, said aggregates or agglomerates having an average diameter D_{50} of between 50 nm and 300 nm (preferably between 100 nm and 200 nm),

it being understood that said material A is selected from the group formed by:

- $TiNb_2O_{7-z}M^3_z$, $Li_wTiNb_2O_{7-z}M^3_z$ wherein M^3 is at least one halogen, preferably selected from F, Cl, Br, I or a mixture thereof, and $0 \leq w \leq 5$ and $0 < z \leq 0.3$;
- $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}La_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}La_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}Cu_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Cu_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$ wherein
  - M^1 and M^2 are at least one element selected from the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs and Sn ;
  - $0 \leq w \leq 5$ and $0 < x < 1$ and $0 \leq y < 2$ and $z \leq 0.3$;
  - $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}$ wherein
    - M^1 is at least one element selected from the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs, Ce and Sn,
    - and wherein $0 \leq w \leq 5$ and $0 < x < 1$ and $0 \leq y < 2$ and $z < 1$, preferably wherein $0 \leq w \leq 5$ and $0 < x < 1$ and $0 \leq y < 2$ and $z < 0.3$;

knowing that said first and/or said second substrate can be a substrate capable of acting as a collector of electric current, or an intermediate substrate,

- a second colloidal suspension is provided comprising aggregates or agglomerates of monodisperse primary nanoparticles of at least one active material of cathode C, with an average primary diameter D_{50} of between 2 and 100 nm, preferably of between 2 and 60 nm, said aggregates or agglomerates having an average diameter D_{50} of between 50 nm and 300 nm (preferably of between 100 nm and 200 nm), and
- a third colloidal suspension is provided comprising aggregates or agglomerates of nanoparticles of at least one inorganic material E, with an average primary diameter D_{50} of between 2 nm and 100 nm, preferably of between 2 nm and 60 nm, said aggregates or agglomerates having an average diameter D50 of between 50 nm and 300 nm (preferably of between 100 nm and 200 nm);

(b) on at least one face of said first substrate an anode layer from said first colloidal suspension supplied in step (a) is deposited, and on at least one face of said second substrate a cathode layer from said second colloidal suspension supplied in step (a) is deposited, by a method selected preferably from the group including: electrophoresis, extrusion, a printing method, selected preferably from inkjet printing and flexographic printing, and a coating method, preferably selected from roll coating, curtain coating, doctor blade coating, coating by extrusion through a slot die, dip coating;

(c) said anode and cathode layers obtained in step (b) are dried, if necessary after having separated said layer from its intermediate substrate, and each layer is consolidated by pressing and/or heating, to obtain respectively a porous, preferably mesoporous and inorganic, anode layer, and a porous, preferably mesoporous and inorganic, cathode layer;

(d) a coating of an electronically conductive material is deposited on and inside the pores of said porous anode and/or cathode layers, so as to form said porous anodes and porous cathodes;

(e) on said porous anode and/or said porous cathode obtained in step (d), a porous inorganic layer from the third colloidal suspension provided in step (a) is deposited by a technique selected from the group including: electrophoresis, extrusion, a printing method, preferably selected from inkjet printing and flexographic printing, and a coating method, preferably selected from roll coating, curtain coating, doctor blade coating, coating by extrusion through a slot die, dip coating;

(f) said porous inorganic layer of the structure obtained in step (e) is dried, preferably under a flow of air, and a heat treatment is carried out at a temperature higher than 130°C and preferably between about 300°C and about 600°C, knowing that if necessary the layer separated from its intermediate substrate is pressed onto a metal sheet capable of acting as a current collector before performing said heat treatment;

(g) the porous anode obtained in step d) or e) is successively stacked face-to-face with the porous cathode obtained in step d) or e), it being understood that the stack obtained comprises at least one porous inorganic layer as obtained in step e) forming said separator;

(h) the stack obtained in step (g) is subjected to a thermocompression treatment at a temperature between 120°C and 600°C in order to obtain a battery comprising at least one porous anode, at least one separator and at least one porous cathode.

14. Method according to claim 13, characterised in that said inorganic material E is an electrical insulator.

15. Method according to claim 13 or 14, wherein the product resulting from step (h) is impregnated with an electrolyte, preferably by a lithium ion carrier phase, selected from the group formed by:

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

and even more preferably, by an electrolyte selected from the group including:

- an electrolyte comprising N-butyl-N-methyl-pyrrolidinium 4,5-dicyano-2-(trifluoromethyl) imidazole ($Pyr_{14}TDI$),
- an electrolyte comprising 1-methyl-3-propylimidazolium 4,5-dicyano-2-(trifluoro-methyl)imidazolide (PMIM-TDI) and lithium 4,5-dicyano-2-(trifluoro-methyl)imidazolide (LiTDI).

16. Method according to any of claims 13 to 15, wherein said active material of cathode C is selected from the group formed by: $LiCoPO_4$, $LiMn_{1,5}Ni_{0.5}O_4$, $LiFe_xCo_{1-x}PO_4$ and where $0 < x < 1$, $LiNi_{1/x}Co_{1/y}Mn_{1/z}O_2$ with $x+y+z = 10$, $Li_{1,2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$, $LiMn_{1,5}Ni_{0.5-x}X_xO_4$ where X is selected from Al, Fe, Cr, Co, Rh, Nd, Sc, Y, Lu, La, Ce, Pr, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and where $0 < x < 0.1$, $LiNi_{0,8}Co_{0.15}Al_{0,05}O_2$, Li_2MPO_4F 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, $LiMSO_4F$ with M = Fe, Co, Ni, Mn, Zn, Mg, $LiCoO_2$.

17. Lithium-ion battery, which can be obtained by the method according to any of claims 12 to 16.

18. Battery according to claim 17, characterised in that its electrolyte liquid contains at least 50% by mass ionic liquid, which is preferably $Pyr_{14}TFSI$.

19. Battery according to any of claims 17 or 18 dependent on any of claims 13 to 16, characterised in that:

- its cathode current collector is made from a material selected from the group including: Mo, Ti, W, Ta, Cr, Al, alloys based on the aforementioned elements, stainless steel;
- its cathode is made of NMC and preferably NMC433, and it has a porous volume of between 30 and 40%, with a conductive layer of carbon deposited in the pores;
- its separator is a mesoporous layer of Li_3PO_4, preferably having a thickness of between 6 µm and 8 µm;
- its anode is a layer of $TiNb_2O_{7-\delta}$, with $0 \leq \delta \leq 0.3$, preferably doped with a halide and/or germanium, said layer being impregnated by a liquid electrolyte containing lithium salts;
- its anode current collector is selected from the group formed by: Mo, Cu, Ni, alloys based on the aforementioned elements, stainless steel.

20. Battery according to any of claims 17 to 19, characterised in that it has electrodes with a thickness greater than 10 µm.

21. Battery according to any of claims 17 to 20, characterised in that it comprises an anode according to claim 10 or 11, or able to be obtained by the method according to any of claims 1 to 9, and in that said anode has a mass capacity greater than 200 mAh/g, and preferably greater than 250 mAh/g.

22. Use of a battery according to any of claims 17 to 20 at a temperature below -10°C or a temperature higher than 50°C.