CLAIMS

1. A method for manufacturing an electrochemical device selected from the group formed by: lithium-ion batteries ~~with a capacity greater than 1 mAh~~, sodium ion batteries, lithium-air batteries, photovoltaic cells, fuel cells,

said method implementing a method for manufacturing an assembly consisting of a porous electrode and a porous separator,

said electrode comprising a porous layer deposited on a substrate, said layer being free of binder, having a porosity comprised between 20% and 60% by volume, preferably between 25% and 50%, and pores with an average diameter of less than 50 nm,

said separator comprising a porous inorganic layer deposited on said electrode, said porous inorganic layer being free of binder, having a porosity comprised between 25% and 60% by volume, preferably between 25% and 50%, and pores with an average diameter of less than 50 nm,

said manufacturing method being characterised in that:

(a) provision is made of a substrate, a first colloidal suspension or a paste comprising aggregates or agglomerates of monodisperse primary nanoparticles of at least one active electrode material P, of average primary diameter D_{50} comprised between 2 nm and 150 nm, preferably between 2 nm and 100 nm, and more preferably comprised between 2 nm and 60 nm, said aggregates or agglomerates having an average diameter D_{50} comprised between 50 nm and 300 nm, preferably between 100 nm and 200 nm, and a second colloidal suspension comprising aggregates or agglomerates of nanoparticles of at least one inorganic material E, having an average primary diameter D_{50} comprised between 2 nm and 100 nm, preferably comprised between 2 nm and 60 nm, said aggregates or agglomerates having an average diameter D_{50} comprised between 50 nm and 300 nm, preferably between 100 nm and 200 nm,

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

(c) said layer obtained in step (b) is dried, where appropriate before or after having separated said layer from its intermediate substrate, then, optionally, said dried layer is heat treated, preferably under an oxidising atmosphere, and it is consolidated, by pressing and/or heating, to obtain a porous, preferably mesoporous and inorganic, layer,

(d) a coating of an electronically conductive material is deposited on and inside the pores of said porous layer, so as to form said porous electrode,

(e) a porous inorganic layer from the second colloidal suspension provided in step (a) is deposited on said porous electrode obtained in step (d), by a technique selected from the group formed of: electrophoresis, a printing method, preferably selected from ink-jet printing and flexographic printing, and a coating method, preferably selected from roll coating, curtain coating, doctor blade coating, extrusion slot-die coating, dip-coating,

(f) said porous inorganic layer of the structure obtained in step (e) is dried, preferably under an air flow, and heat treatment is carried out at a temperature below 500°C, preferably at approximately 400°C in order to obtain said assembly consisting of a porous electrode and a porous separator,

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

2. The method according to claim 1, characterised in that said porous layer obtained at the end of step (c) has a specific surface comprised between 10 m^2/g and 500 m^2/g.

3. The method according to any one of claims 1 or 2, characterised in that said porous layer obtained at the end of step (c) has a thickness comprised between 4 µm and 400 µm.

4. The method according to any one of claims 1 to 3, characterised in that when said substrate is an intermediate substrate, said layer is separated in step (c) before or after its drying from said intermediate substrate, to form a porous plate.

5. The method, characterised in that when said colloidal suspension or paste provided in step (a) comprises organic additives, such as ligands, stabilisers, binders or residual organic solvents, said layer dried in step c) according to any one of claims 1 to 3, or said porous plate according to claim 4, is heat treated, preferably under an oxidising atmosphere.

6. The method according to any one of claims 1 to 5, characterised in that said porous inorganic layer obtained at the end of step (f) has a thickness comprised between 3 µm and 20 µm, and preferably between 5 µm and 10 µm.

7. The method according to any one of claims 1 to 6, characterised in that said electronically conductive material is carbon.

8. The method according to any one of claims 1 to 7, characterised in that the deposition of said coating of electronically conductive material is carried out by the atomic layer deposition technique, or by immersion in a liquid phase including a precursor of said

electronically conductive material, followed by the transformation of said precursor into electronically conductive material.

9. The method according to claim 8, characterised in that said precursor is a carbon-rich compound, such as a carbohydrate, preferably a polysaccharide, and in that said transformation into an electronically conductive material is done by pyrolysis, preferably under an inert atmosphere.

10. The method according to any one of claims 1 to 9, wherein said material P is selected from the group formed of:

- oxides $LiMn_2O_4$, $Li_{1+x}Mn_{2-x}O_4$ with $0 < x < 0.15$, $LiCoO_2$, $LiNiO_2$, $LiMn_{1.5}Ni_{0.5}O_4$, $LiMn_{1.5}Ni_{0.5-x}X_xO_4$ 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 $0 < x < 0.1$, $LiMn_{2-x}M_xO_4$ with M = Er, Dy, Gd, Tb, Yb, Al, Y, Ni, Co, Ti, Sn, As, Mg or a mixture of these elements and where $0 < x < 0.4$, $LiFeO_2$, $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $LiAl_xMn_{2-x}O_4$ with $0 \leq x < 0.15$, $LiNi_{1/x}Co_{1/y}Mn_{1/z}O_2$ with $x+y+z = 10$;
- $Li_xM_yO_2$ where $0.6 \leq y \leq 0.85$; $0 \leq x+y \leq 2$; and M is selected from Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Sn, and Sb or a mixture of these elements; $Li_{1.20}Nb_{0.20}Mn_{0.60}O_2$;
- $Li_{1+x}Nb_yMe_zA_pO_2$ where Me is at least one transition metal selected from: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Rf, Db, Sg, Bh, Hs and Mt, and where $0.6<x<1$; $0<y<0.5$; $0.25 \leq z<1$; with A ≠ Me and A ≠ Nb, and $0 \leq p \leq 0.2$;
- $Li_xNb_{y-a}N_aM_{z-b}P_bO_{2-c}F_c$ where $1.2<x \leq 1.75$; $0 \leq y<0.55$; $0.1<z<1$; $0 \leq a<0.5$; $0 \leq b<1$; $0 \leq c<0.8$; and where M, N, and P are each at least one of the elements selected from the group consisting of Ti, Ta, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Zr, Y, Mo, Ru, Rh, and Sb;
- $Li_{1.25}Nb_{0.25}Mn_{0.50}O_2$; $Li_{1.3}Nb_{0.3}Mn_{0.40}O_2$; $Li_{1.3}Nb_{0.3}Fe_{0.40}O_2$; $Li_{1.3}Nb_{0.43}Ni_{0.27}O_2$; $Li_{1.3}Nb_{0.43}Co_{0.27}O_2$; $Li_{1.4}Nb_{0.2}Mn_{0.53}O_2$;
- $Li_xNi_{0.2}Mn_{0.6}O_y$ where $0.00 \leq x \leq 1.52$; $1.07 \leq y<2.4$; $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$;
- $LiNi_xCo_yMn_{1-x-y}O_2$ where $0 \leq x$ and $y \leq 0.5$; $LiNi_xCe_zCo_yMn_{1-x-y}O_2$ where $0 \leq x$ and $y \leq 0.5$ and $0 \leq z$; phosphates $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$, $LiNiPO_4$, $Li_3V_2(PO_4)_3$; 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; the phosphates of formula LiMM'PO_4, with M and M' (M ≠ M') selected from Fe, Mn, Ni, Co, V such as the $LiFe_xCo_{1-x}PO_4$ and where $0 < x < 1$;
- oxyfluorides of the type $Fe_{0.9}Co_{0.1}OF$; $LiMSO_4F$ with M = Fe, Co, Ni, Mn, Zn, Mg;

- all lithiated forms of the following chalcogenides: V_2O_5, V_3O_8, TiS_2, titanium oxysulfides (TiO_yS_z with z=2-y and 0.3≤y≤1), tungsten oxysulfides (WO_yS_z with 0.6<y<3 and 0.1<z<2), CuS, CuS_2, preferably $Li_xV_2O_5$ with 0 <x≤2, $Li_xV_3O_8$ with 0 < x ≤ 1.7, Li_xTiS_2 with 0 < x ≤ 1, titanium and lithium oxysulfides with $Li_xTiO_yS_z$ with z=2-y, 0.3≤y≤1 and 0 < x ≤ 1, $Li_xWO_yS_z$ with z=2-y, 0.3≤y≤1 and 0 < x ≤ 1, Li_xCuS with 0 < x ≤ 1, Li_xCuS_2 with 0 < x ≤ 1.

11. The method according to any one of claims 1 to 7, wherein said material P is selected from the group formed of:

- $Li_4Ti_5O_{12}$, $Li_4Ti_{5-x}M_xO_{12}$ with M = V, Zr, Hf, Nb, Ta and 0 ≤ x ≤ 0.25.
- niobium oxides and mixed niobium oxides with titanium, germanium, cerium or tungsten, and preferably from the group formed of:
  - $Nb_2O_{5\pm\delta}$, $Nb_{18}W_{16}O_{93\pm\delta}$, $Nb_{16}W_5O_{55\pm\delta}$ with 0 ≤ x < 1 and 0 ≤ δ ≤ 2, $LiNbO_3$,
  - $TiNb_2O_{7\pm\delta}$, $Li_wTiNb_2O_7$ with w≥0, $Ti_{1-x}M^1_xNb_{2-y}M^2_yO_{7\pm\delta}$ or $Li_wTi_{1-x}M^1_xNb_{2-y}M^2_yO_{7\pm\delta}$ wherein M^1 and M^2 are each at least one element selected from the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs and Sn, M^1 and M^2 can be identical or different from each other, and wherein 0 ≤ w ≤ 5 and 0 ≤ x ≤ 1 and 0 ≤ y ≤ 2 and 0 ≤ δ ≤ 0.3;
  - $La_xTi_{1-2x}Nb_{2+x}O_7$ where 0<x<0.5;
  - $M_xTi_{1-2x}Nb_{2+x}O_{7\pm\delta}$
    - wherein M is an element whose degree of oxidation is +III, more particularly M is at least one of the elements selected from the group consisting of Fe, Ga, Mo, Al, B, and where 0<x≤0.20 and -0.3≤ δ ≤0.3; $Ga_{0.10}Ti_{0.80}Nb_{2.10}O_7$; $Fe_{0.10}Ti_{0.80}Nb_{2.10}O_7$;
  - $M_xTi_{2-2x}Nb_{10+x}O_{29\pm\delta}$
    - wherein M is an element whose degree of oxidation is +III, more particularly M is at least one of the elements selected from the group consisting of Fe, Ga, Mo, Al, B, and where 0<x≤0.40 and -0.3≤ δ ≤0.3;
- $Ti_{1-x}M^1_xNb_{2-y}M^2_yO_{7-z}M^3_z$ or $Li_wTi_{1-x}M^1_xNb_{2-y}M^2_yO_{7-z}M^3_z$ wherein
  - M^1 and M^2 are each at least one element selected from the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs and Sn,
  - M^1 and M^2 can be identical or different from each other,
  - 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 $z \leq 0.3$;

- $TiNb_2O_{7-z}M^3_z$ or $Li_wTiNb_2O_{7-z}M^3_z$ wherein M^3 is at least one halogen, preferably selected from F, Cl, Br, I or a mixture thereof, and $0 < z \leq 0.3$;
- $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7\pm z}$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7\pm z}$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7\pm z}$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7\pm z}$ wherein
  - 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 $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$;
- $Ti_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ge_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Ti_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$, $Li_wTi_{1-x}Ce_xNb_{2-y}M^1_yO_{7-z}M^2_z$, wherein
  - M^1 and M^2 are each at least one element selected from the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs, Ce and Sn,
  - M^1 and M^2 can be identical or different from each other,
  - and wherein $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $z \leq 0.3$
- TiO_2;
- LiSiTON.

12. The method according to any one of claims 1 to 11, wherein said inorganic material E comprises an electronically insulating material, preferably selected from:

- Al_2O_3, SiO_2, ZrO_2, and/or
- a material selected from the group formed of lithiated phosphates, preferably selected from: lithiated phosphates of the NaSICON type, Li_3PO_4; $LiPO_3$; $Li_3Al_{0.4}Sc_{1.6}(PO_4)_3$ called "LASP"; $Li_{1+x}Zr_{2-x}Ca_x(PO_4)_3$ with $0 \leq x \leq 0.25$; $Li_{1+2x}Zr_{2-x}Ca_x(PO_4)_3$ with $0 \leq x \leq 0.25$ such as $Li_{1.2}Zr_{1.9}Ca_{0.1}(PO_4)_3$ or $Li_{1.4}Zr_{1.8}Ca_{0.2}(PO_4)_3$; $LiZr_2(PO_4)_3$; $Li_{1+3x}Zr_2(P_{1-x}Si_xO_4)_3$ with $1.8 < x < 2.3$; $Li_{1+6x}Zr_2(P_{1-x}B_xO_4)_3$ with $0 \leq x \leq 0.25$; $Li_3(Sc_{2-x}M_x)(PO_4)_3$ with M=Al or Y and $0 \leq x \leq 1$; $Li_{1+x}M_x(Sc)_{2-x}(PO_4)_3$ with M = Al, Y, Ga or a mixture of these three elements and $0 \leq x \leq 0.8$; $Li_{1+x}M_x(Ga_{1-y}Sc_y)_{2-x}(PO_4)_3$ with $0 \leq x \leq 0.8$; $0 \leq y \leq 1$ and M= Al and/or Y; $Li_{1+x}M_x(Ga)_{2-x}(PO_4)_3$ with M = Al and/or Y and $0 \leq x \leq 0.8$; $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ with $0 \leq x \leq 1$ called "LATP"; or $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ with $0 \leq x \leq 1$ called "LAGP"; or $Li_{1+x+z}M_x(Ge_{1-y}Ti_y)_{2-x}Si_zP_{3-z}O_{12}$ with $0 \leq x \leq 0.8$ and $0 \leq y \leq 1.0$ and $0 \leq z \leq 0.6$ and M= Al, Ga or Y or a mixture of two or three of these elements; $Li_{3+y}(Sc_{2-x}M_x)Q_yP_{3-y}O_{12}$ with M = Al and/or Y and Q = Si and/or Se, $0 \leq x \leq 0.8$ and $0 \leq y \leq 1$; or $Li_{1+x+y}M_xSc_{2-x}Q_yP_{3-y}O_{12}$ with M = Al, Y, Ga or a mixture of these three elements and Q = Si and/or Se, $0 \leq x \leq 0.8$ and

$0 \leq y \leq 1$; or $Li_{1+x+y+z}M_x(Ga_{1-y}Sc_y)_{2-x}Q_zP_{3-z}O_{12}$ with $0 \leq x \leq 0.8$, $0 \leq y \leq 1$, $0 \leq z \leq 0.6$ with M = Al and/or Y and Q= Si and/or Se; or $Li_{1+x}Zr_{2-x}B_x(PO_4)_3$ with $0 \leq x \leq 0.25$; or $Li_{1+x}M^3{}_xM_{2-x}P_3O_{12}$ with $0 \leq x \leq 1$ and M^3= Cr, V, Ca, B, Mg, Bi and/or Mo, M = Sc, Sn, Zr, Hf, Se or Si, or a mixture of these elements.

13. The method according to any one of claims 1 to 12, characterised in that said assembly consisting of a porous electrode and a porous separator is impregnated with an electrolyte, preferably a phase carrying lithium ions, selected from the group formed of:

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

said polymer being preferably selected from the group formed of poly(ethylene oxide), poly(propylene oxide), polydimethylsiloxane, polyacrylonitrile, poly(methyl methacrylate), poly(vinyl chloride), poly(vinylidene fluoride), PVDF-hexafluoropropylene.

14. The method according to any one of claims 1 to 13 wherein the method for manufacturing an assembly consisting of a porous electrode and a separator according to claim 8 is implemented to manufacture an assembly said electrode of which is a positive electrode.

15. The method according to any one of claims 1 to 14, wherein the method according to claim 9 is implemented to manufacture an assembly said electrode of which is a negative electrode.

16. The method according to any one of claims 14 to 15, wherein said assembly consisting of a porous electrode and a separator is impregnated with an electrolyte, preferably a phase carrying lithium ions, selected from the group formed of:

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

said polymer being preferably selected from the group formed of poly(ethylene oxide), poly(propylene oxide), polydimethylsiloxane, polyacrylonitrile, poly(methyl methacrylate), poly(vinyl chloride), poly(vinylidene fluoride), PVDF-hexafluoropropylene.

17. A lithium-ion battery ~~with a capacity greater than 1 mAh,~~ that can be obtained by the method according to any one of claims 1 to 16.

18. An electrochemical device selected from the group formed by sodium ion batteries, lithium-air batteries, fuel cells and photovoltaic cells, that can be obtained by the manufacturing method according to any one of claims 1 to 16.