CLAIMS

1. A method for manufacturing a porous electrode, in particular for electrochemical devices, said electrode comprising a porous layer deposited on a substrate, said layer being free of binder, having a porosity comprised between 20% and 60% by volume, preferably between 25% and 50%, and pores with an average diameter of less than 50 nm, said manufacturing method being characterised in that:

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

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

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

(d) depositing, on and inside the pores of said porous layer, a coating of an electronically conductive material,

said substrate being either a substrate capable of acting as an electric current collector or an intermediate substrate.

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

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

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

5. The method, characterised in that when said colloidal suspension or paste provided in step (a) comprises organic additives, such as ligands, stabilisers, binders or residual organic solvents, said layer dried in step c) is heat treated, preferably under an oxidising

atmosphere, according to any one of claims 1 to 3, or said porous plate according to claim 4.

6. The method according to any one of claims 1 to 5, characterised in that said electronically conductive material is carbon.

7. The method according to any one of claims 1 to 6, characterised in that the deposition of said coating of electronically conductive material is carried out by the atomic layer deposition ALD technique or by immersion of the porous layer in a liquid phase including a precursor of said electronically conductive material, followed by the transformation of said precursor into electronically conductive material.

8. The method according to claim 7, characterised in that said precursor is a carbon-rich compound, such as a carbohydrate, preferably a polysaccharide, and in that said transformation into an electronically conductive material is a pyrolysis, preferably under an inert atmosphere.

9. The method according to any one of claims 1 to 8, wherein said material P is selected from the group formed of:

- the 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 compounds 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' ($M \neq M'$) selected from Fe, Mn, Ni, Co, V such as the $LiFe_xCo_{1-x}PO_4$ and where $0 < x < 1$;
- $Fe_{0.9}Co_{0.1}OF$; $LiMSO_4F$ 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 $0.3 \leq y \leq 1$), tungsten oxysulfides (WO_yS_z with $0.6<y<3$ and $0.1<z<2$), CuS, CuS_2, preferably $Li_xV_2O_5$ with $0 <x \leq 2$, $Li_xV_3O_8$ with $0 < x \leq 1.7$, Li_xTiS_2 with $0 < x \leq 1$, titanium and lithium oxysulfides with $Li_xTiO_yS_z$ with z=2-y, $0.3 \leq y \leq 1$ and $0 < x \leq 1$, $Li_xWO_yS_z$ with z=2-y, $0.3 \leq y \leq 1$ and $0 < x \leq 1$, Li_xCuS with $0 < x \leq 1$, Li_xCuS_2 with $0 < x \leq 1$.

10. The method according to any one of claims 1 to 8, wherein said material P is selected from the group formed of:

- $Li_4Ti_5O_{12}$, $Li_4Ti_{5-x}M_xO_{12}$ with M = V, Zr, Hf, Nb, Ta and $0 \leq x \leq 0.25$;
- niobium oxides and mixed 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 $0 \leq x < 1$ and $0 \leq \delta \leq 2$, $LiNbO_3$,
  - $TiNb_2O_{7\pm\delta}$, $Li_wTiNb_2O_7$ with $w \geq 0$, $Ti_{1-x}M^1_xNb_{2-y}M^2_yO_{7\pm\delta}$ 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 $0 \leq w \leq 5$ and $0 \leq x \leq 1$ and $0 \leq y \leq 2$ and $0 \leq \delta \leq 0.3$;
  - $La_xTi_{1-2x}Nb_{2+x}O_7$ 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 $0<x\leq 0.20$ and $-0.3\leq \delta \leq 0.3$; $Ga_{0.10}Ti_{0.80}Nb_{2.10}O_7$; $Fe_{0.10}Ti_{0.80}Nb_{2.10}O_7$;
  - $M_xTi_{2-2x}Nb_{10+x}O_{29\pm\delta}$
    - 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 $0<x\leq 0.40$ and $-0.3\leq \delta \leq 0.3$;
  - $Ti_{1-x}M^1_xNb_{2-y}M^2_yO_{7-z}M^3_z$ 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 is at least one element selected from the group consisting of Nb, V, Ta, Fe, Co, Ti, Bi, Sb, As, P, Cr, Mo, W, B, Na, Mg, Ca, Ba, Pb, Al, Zr, Si, Sr, K, Cs and Sn;
  - $0 \leq w \leq 5$ 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.

11. A porous electrode having a porosity comprised between 20% and 60% by volume, free of binder, comprising pores with an average diameter of less than 50 nm.

12. A use of a method according to any one of claims 1 to 10 for manufacturing porous electrodes in lithium-ion batteries.

13. A method for manufacturing a battery, implementing the method for manufacturing a porous electrode according to one of claims 1 to 10, or implementing a porous electrode according to claim 11.

14. The method according to claim 13, characterised in that said battery is a lithium-ion battery.

15. The method according to claim 13 or 14, wherein the method for manufacturing a porous electrode according to claim 11 is implemented to manufacture a cathode or the method according to claim 11 is implemented to manufacture an anode.

16. The method according to any one of claims 13 to 15, wherein said porous electrode is impregnated with an electrolyte, preferably a phase carrying lithium ions selected from the group formed of:

- 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 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.

17. A lithium-ion battery comprising a porous electrode having a porosity comprised between 20% and 60% by volume, free of binder, comprising pores with an average diameter of less than 50.