CLAIMS

1. A method for producing a porous electrode, said electrode comprising a layer deposited on a substrate, said layer being binder-free and having a porosity of more than 30 volume %, and preferably less than 50 volume %, and pores having an average diameter of less than 50 nm, said method being characterized in that:
   (a) A colloidal suspension is provided, containing aggregates or agglomerates of nanoparticles of at least one material P having an average primary diameter D_{50} of less than or equal to 80 nm, and preferably less than or equal to 50 nm, said aggregates or agglomerates having an average diameter comprised between 80 nm and 300 nm (preferably between 100 nm and 200 nm); wherein the “average primary diameter” refers to the average diameter of the non-aggregated or non-agglomerated nanoparticles,
   (b) a substrate is provided,
   (c) a porous, preferably mesoporous, electrode layer is deposited on said substrate by electrophoresis, by ink-jet, by doctor blade, by roll coating, by curtain coating or by dip-coating, from said colloidal suspension provided in step (a);
   (d) said layer obtained in step (c) is dried, preferably in an air flow,
   (e) optionally, consolidation of the porous, preferably mesoporous electrode layer obtained in step (d) by pressing and/or heating.

2. The method according to claim 1, wherein:

   (a1) a colloidal suspension is provided including nanoparticles of at least one material P with a primary diameter D_{50} less than or equal to 80 nm, and preferably less than or equal to 50 nm;

   (a2) the nanoparticles present in said colloidal suspension are destabilized so as to form aggregates or agglomerates of particles with an average diameter comprised between 80 nm and 300 nm, preferably between 100 nm and 200 nm, said destabilization being done preferably by adding a destabilizing agent such as a salt, preferably LiOH;

   (b) a substrate is provided;

   (c) a mesoporous electrode layer is deposited on said substrate by electrophoresis, by ink-jet, by doctor blade, by roll coating, by curtain

coating or by dip-coating, from said colloidal suspension comprising the aggregates or agglomerates of nanoparticles obtained in step (a2);

(d) said layer is dried, preferably in an air flow;

(e) optionally, consolidation of the mesoporous electrode layer obtained in step (d) by pressing and/or heating.

3. The method according to claim 1 or 2, wherein the deposition obtained in step (c) has a thickness less than 10 µm, preferably less than 8 µm, and even more preferably comprised between 1 µm and 6 µm.

4. The method according to one of claims 1 to 3, wherein the diameter of said nanoparticles is comprised between 10 nm and 50 nm, preferably between 10 nm and 30 nm.

5. The method according to one of claims 1 to 4, wherein the average diameter of the pores is comprised between 2 nm and 80 nm, preferably comprised between 2 nm and 50 nm, preferably comprised between 6 nm and 30 nm and even more preferably between 8 nm and 20 nm.

6. The method according to any of the preceding claims, wherein the porous electrode has a porosity comprised between 35% and 50% by volume, and more preferably between 40% and 50% by volume.

7. The method according to any of claims 1 to 6, wherein said electrode is a cathode, and said material P is chosen from the group formed by:
   - 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;
   - phosphates $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$, $LiNiPO_4$, $Li_3V_2(PO_4)_3$; phosphates of formula $LiMM'PO_4$, with M and M' ($M \neq M'$) selected from Fe, Mn, Ni, Co, V;

- all lithium 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 oxysulfides and lithium oxysulfides $Li_xTiO_yS_z$ with z=2-y, 0.3≤y≤1, $Li_xWO_yS_z$, Li_xCuS, Li_xCuS_2.

8. The method according to any of claims 1 to 7, wherein said electrode is an anode, and said material P is chosen from the group formed by:
   - carbon nanotubes, graphene, graphite;
   - lithium iron phosphate (of typical formula $LiFePO_4$);
   - silicon and tin oxinitrides (of typical formula $Si_aSn_bO_yN_z$ with a>0, b>0, a+b≤2, 0<y≤4, 0<z≤3) (also called SiTON), and in particular $SiSn_{0.87}O_{1.2}N_{1.72}$; as well as the oxynitride-carbides of typical formula $Si_aSn_bC_cO_yN_z$ with a>0, b>0, a+b≤2, 0<c<10, 0<y<24, 0<z<17;
   - nitrides of the 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≤x≤0.5 for M=Co, 0≤x≤0.6 for M=Ni, 0≤x≤0.3 for M=Cu); $Si_{3-x}M_xN_4$ with M=Co or Fe and 0≤x≤3.
   - oxides SnO_2, SnO, Li_2SnO_3, $SnSiO_3$, Li_xSiO_y (x>=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,
   - composite oxides $TiNb_2O_7$ comprising between 0% and 10% carbon by weight, preferably carbon being chosen from graphene and the carbon nanotubes.

9. The method according to any of the preceding claims, wherein after step (d) or step (e) is deposited, preferably by atomic layer deposition ALD or chemically in a solution CSD, during a step (f) a layer of electrically-insulating material on and inside the pores of the porous layer.

10. The method according to claim 9, wherein the electrically-insulating material is chosen from Al_2O_3, SiO_2, ZrO_2.

11. The method according to any of claims 1 to 8, wherein after step (d) or after step (e), is deposited preferably by ALD or by CSD, during a step (f) a layer of ionic conductive material chosen from Li_3PO_4, Li_3BO_3, lithium lanthanum zirconium oxide, preferably $Li_7La_3Zr_2O_{12}$, on and inside the pores of the porous layer.

12. Use of a method according to any one of claims 1 to 11 for the manufacture of porous electrodes, in electronic, electrical or electrotechnical devices and preferably in devices selected in the group composed of batteries, capacitors, supercapacitors, capacities, resistors, inductors, transistors, photovoltaic cells.

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

14. A process for manufacturing a battery according to claim 13 and comprising the steps of:

(1) Providing a colloidal suspension comprising aggregates or agglomerates of nanoparticles of at least one cathode material with an average primary diameter D_{50} less than or equal to 50 nm;

(2) Providing a colloidal suspension comprising aggregates or agglomerates of nanoparticles of at least one anode material with an average primary diameter D_{50} less than or equal to 50 nm.

(3) Providing of at least two flat conducting substrates, preferably metal, said conducting substrates can be used as current collectors of the battery,

(4) Deposition of at least one layer of cathode, respectively anode, by dip-coating, by ink-jet, by doctor blade, by roll coating, by curtain coating or by electrophoresis, preferably by pulsed-current galvanostatic electrodeposition, from said suspension of nanoparticles of material provided in step (1), respectively in step (2), on said substrate provided in step (3),

(5) Drying the layer thus obtained in the step (4),

(6) Optionally, deposition by ALD of a layer of electrically-insulating material on and inside pores of the layer of cathode, and/or of anode in step (5),

(7) Deposition of a film, preferably porous, preferably mesoporous, of an electrically-insulating material or of an ion-conducting material or of an electrically-insulating material possibly ion-conducting from a colloidal suspension of nanoparticles of this aggregated or agglomerated material of average primary diameter D_{50} less than or equal to 50 nm and of an average diameter D_{50} of 100 nm on the layer of cathode, respectively anode obtained in step (5) and/or step (6); wherein the “average primary diameter” refers to the average diameter of the non-aggregated or non-agglomerated nanoparticles,

(8) Drying the layer thus obtained in the step (7),

(9) Realization of a stack comprising an alternating succession of layers of cathode and anode, preferably offset laterally,

(10) Hot pressing of the layers of anode and cathode obtained in step (9) in such a way as to juxtapose the films obtained in step (8) present on the layers of anode and cathode, and to obtain an assembled stack,

(11) Impregnation of the structure obtained in step (10) by a phase carrying lithium ions leading to the obtaining of an impregnated structure.

15. The process according to claim 14, wherein between step -10- and -11-:

- is deposited successively, alternating, on the assembled stack, an encapsulation system formed by a succession of layers, namely a sequence, preferably z sequences, comprising:
  - a first covering layer, preferably chosen from parylene, parylene of the F type, polyimide, epoxy resins, silicone, polyamide and/or a mixture of the latter, deposited on the assembled stack,
  - a second covering layer comprised of an electrically-insulating material, deposited by atomic layer deposition on said first covering layer,
  - this sequence can be repeated z times with $z \geq 1$,
- a last covering layer is deposited in this succession of layers of a material chosen from epoxy resin, polyethylene naphtalate (PEN), polyimide, polyamide, polyurethane, silicone, sol-gel silica or organic silica,
- the assembled stack thus encapsulated is cut along two cutting planes to expose on each one of the cutting plans anode and cathode connections of the assembled stack, in such a way that the encapsulation system covers four of the six faces of said assembled stack, preferably continuously, in such a way as to obtain an elementary battery,

and after step -11-,

- is deposited successively, on and around, these anode and cathode connections:
  - a first layer of a material charged with graphite, preferably epoxy resin charged with graphite,
  - a second layer comprising metal copper obtained from an ink charged with nanoparticles of copper deposited on the first layer,

- the layers obtained are thermally treated, preferably by infrared flash lamp in such a way as to obtain a covering of the cathode and anode connections by a layer of metal copper,
- possibly, is deposited successively, on and around, this layer of metal copper:
    - a first layer of a tin-zinc alloy deposited, preferably by dipping in a molten tin-zinc bath, so as to ensure the tightness of the battery at least cost, and
    - a second layer with a pure tin base deposited by electrodeposition or a second layer comprising an alloy with a silver, palladium and copper base deposited on this first layer of a tin-zinc alloy.

16. The process according to claim 15, wherein the anode and cathode connections are on the opposite sides of the stack.

17. A porous electrode with a porosity greater than 30% by volume comprising pores with an average diameter less than 80 nm, preferably less than 50 nm, a primary particle diameter less than 30 nm, characterized in that it comprises a thickness less than 100 µm, preferably less than 50 µm and more preferably less than 10 µm and is binder-free.

18. The porous electrode according to claim 17, characterized in that said pores are impregnated, by an electrolyte, preferably a phase carrying lithium ions such as an ionic liquid containing lithium salts, possibly diluted with an organic solvent or a mixture of organic solvents containing a lithium salt that can be different from the one dissolved in the ionic liquid.

19. The porous electrode according to claim 18, characterized in that said pores are impregnated with a phase carrying lithium ions comprising at least 50% by weight of at least one ionic liquid.

20. A battery comprising at least one porous electrode, wherein said porous electrode has a porosity of more than 30% by volume comprising pores with an average diameter less than 80 nm, and is binder-free; wherein said porosity is a homogeneous porosity.

21. The battery according to claim 20, characterized in that all of its electrodes are porous electrodes having a porosity greater than 30% by volume comprising pores

with an average diameter less than 80 nm, and is binder-free; wherein said porosity is a homogeneous porosity.

22. The battery according to claim 20 or 21, wherein the average diameter of the pores is less than 50 nm, with a primary particle diameter less than 30 nm, characterized in that the porous electrode comprises a thickness less than 100 µm, preferably less than 50 µm and more preferably less than 10 µm.

23. The battery according to any one of claims 20 to 22, wherein the porous electrode has a controlled and open porosity.