CLAIMS

1. Method for manufacturing an anodic member for a lithium-ion battery, said battery comprising at least one cathode, at least one electrolyte and at least one anode,

said anode comprising:

- a substrate;
- said anodic member, comprising a porous layer disposed on the substrate, said porous layer having a porosity of between 35% and 70% by volume, and
- metallic lithium loaded inside the pores of said porous layer,

said method comprising the following steps:

(a) a substrate is provided, and a colloidal suspension comprising aggregates or agglomerates of monodisperse nanoparticles of at least one first electrically insulating material conducting lithium ions with a mean primary diameter D_{50} of between 5 nm and 100 nm, said aggregates or agglomerates having a mean diameter of less than 500 nm;

(b) a porous layer is deposited on said surface of said substrate by a method selected from the group formed by electrophoresis, the ink-jet printing method, doctor blade, spraying, flexographic printing, roll coating, curtain coating, slot-die coating and the dip coating method, using said colloidal sustension provided at step (a), on the understanding that said substrate may be a substrate capable of acting as a collector of electrical current of the battery or an intermediate substrate;

(c) said porous layer obtained at step (b) is dried, preferably under a flow of air, where applicable before or after having separated said porous layer from its intermediate substrate, and then, optionally, a heat treatment of the dried layer is implemented.

2. Method for manufacturing an anodic member according to claim 1, wherein said substrate is an intermediate substrate, and wherein also, in step (a), the following are provided

- at least one electrically conductive sheet can serve as a current collector of the battery,
- a conductive glue or a colloidal suspension comprising monodisperse nanoparticles of at least one second material conducting lithium ions with a mean primary diameter D_{50} of between 5 nm and 100 nm;

and, after separation of said porous layer from its intermediate substrate, a heat treatment of the porous layer is implemented, and then, on at least one face, preferably on both faces, of said electrically conductive sheet, a thin layer of conductive glue or a thin layer of

nanoparticles is deposited from the colloidal suspension comprising monodisperse nanoparticles of at least one second material conducting lithium ions, the second material conducting lithium ions preferably being identical to the first material conducting lithium ions; then the porous layer is adhesively bonded on said face, preferably on both faces of said electrically conductive sheet.

3. Method for manufacturing an anodic member according to claim 1 or claim 2, wherein, after step (c), a layer of a lithiophilic material is deposited on and inside the pores of the porous layer, preferably by the atomic layer deposition ALD technique or by chemical solution deposition CSD method, in a step (d).

4. Method for manufacturing an anodic member according to claim 3, wherein the lithiophilic material is selected from ZnO, Al, Si, CuO.

5. Method for manufacturing an anodic member according to any one of the preceding claims, wherein the metal substrate is selected from copper and nickel strips, molybdenum strips, alloy strips comprising at least copper or nickel or chromium.

6. Method for manufacturing an anodic member according to any one of the preceding claims, wherein the primary diameter of said monodisperse nanoparticles is between 10 nm and 50 nm, preferably between 10 nm and 30 nm.

7. Method for manufacturing an anodic member according to any one of the preceding claims, wherein the mean diameter of the pores of the porous layer is between 2 nm and 500 nm, preferably between 2 nm and 80 nm, preferentially between 6 nm and 50 nm, and even more preferentially between 8 nm and 30 nm.

8. Method for manufacturing an anodic member according to any one of the preceding claims, wherein the porous layer has a porosity of approximately 50% by volume.

9. Method for manufacturing an anodic member according to any one of claims 1 to 8, wherein said material conducting lithium ions is selected from the group formed by:

- lithiated phosphates, preferably selected from: lithiated phosphates of the following types: NaSICON, 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 $1.8 < x < 2.3$; $Li_{1+6x}Zr_2(P_{1-x}B_xO_4)_3$ $0 \leq x \leq 0.25$; $Li_3(Sc_{2-x}M_x)(PO_4)_3$ 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 the three compounds 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 or Y or a mixture of the two compounds; $Li_{1+x}M_x(Ga)_{2-x}(PO_4)_3$ with M = Al, Y or a mixtures of the two compounds and $0 \leq x \leq 0.8$; $Li_{3+y}(Sc_{2-x}M_x)Q_yP_{3-y}O_{12}$ 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 the three compounds 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 or Y or a mixture of the two compounds 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 $Li_{1+x}Zr_{2-x}Ca_x(PO_4)_3$ 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 compounds;

- lithiated borates, preferably selected from: $Li_3(Sc_{2-x}M_x)(BO_3)_3$ with M=Al or Y and $0 \leq x \leq 1$; le $Li_{1+x}M_x(Sc)_{2-x}(BO_3)_3$ with M = Al, Y, Ga or a mixture of the three compounds and $0 \leq x \leq 0.8$; $Li_{1+x}M_x(Ga_{1-y}Sc_y)_{2-x}(BO_3)_3$ with $0 \leq x \leq 0.8$, $0 \leq y \leq 1$ and M= Al or Y; $Li_{1+x}M_x(Ga)_{2-x}(BO_3)_3$ with M = Al, Y or a mixture of the two compounds and $0 \leq x \leq 0.8$; Li_3BO_3, Li_3BO_3-Li_2SO_4, Li_3BO_3-Li_2SiO_4, Li_3BO_3-Li_2SiO_4-Li_2SO_4; $Li_3Al_{0,4}Sc_{1,6}(BO_3)_3$; $Li_{1+x}Zr_{2-x}Ca_x(BO_3)_3$ with $0 \leq x \leq 0.25$; $Li_{1+2x}Zr_{2-x}Ca_x(BO_3)_3$ with $0 \leq x \leq 0.25$ such as $Li_{1.2}Zr_{1.9}Ca_{0.1}(BO_3)_3$ or $Li_{1.4}Zr_{1.8}Ca_{0.2}(BO_3)_3$; $LiZr_2(BO_3)_3$; $Li_{1+3x}Zr_2(B_{1-x}Si_xO_3)_3$ with $1,8 < x < 2.3$; $Li_{1+6x}Zr_2(P_{1-x}B_xO_4)_3$ with $0 < x \leq 0.25$; $Li_3(Sc_{2-x}M_x)(BO_3)_3$ with M=Al and/or Y and $0 \leq x \leq 1$; $Li_{1+x}M_x(Sc)_{2-x}(BO_3)_3$ with M = Al, Y, Ga or a mixture of these three elements and $0 \leq x \leq 0.8$; $Li_{1+x}M_x(Ga_{1-y}Sc_y)_{2-x}(BO_3)_3$ with $0 \leq x \leq 0.8$; $0 \leq y \leq 1$ and M= Al and/or Y; $Li_{1+x}M_x(Ga)_{2-x}(BO_3)_3$ with M = Al and/or Y $0 \leq x \leq 0.8$; $Li_{3+y}(Sc_{2-x}M_x)Q_yB_{3-y}O_9$ 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 $Li_{1+x+y}M_xSc_{2-x}Q_yB_{3-y}O_9$ with M = Al, Y, Ga or a mixture of these three element and Q = Si and/or Se, $0 \leq x \leq 0.8$ and $0 \leq y \leq 1$; or $Li_{1+x+y+z}M_x(Ga_{1-y}Sc_y)_{2-x}Q_zB_{3-z}O_9$ 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 $Li_{1+x}Zr_{2-x}B_x(BO_3)_3$ with $0 \leq x \leq 0.25$; or $Li_{1+x}Zr_{2-x}Ca_x(BO_3)_3$ with $0 \leq x \leq 0.25$; or $Li_{1+x}M^3{}_xM_{2-x}(BO_3)_3$ 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;
- oxynitrides, preferably selected from $Li_3PO_{4-x}N_{2x/3}$ and $Li_3BO_{3-x}N_{2x/3}$ with $0 < x < 3$;
- lithiated compounds based on lithium phosphorus oxynitride, called “LiPON”, in the form of $Li_xPO_yN_z$ with $x \sim 2.8$ and $2y + 3z \sim 7.8$ and $0.16 \leq z \leq 0.4$, and in particular $Li_{2,9}PO_{3,3}N_{0,46}$, but also the compounds $Li_wPO_xN_yS_z$ with $2x + 3y + 2z = 5 = w$ or the compounds $Li_wPO_xN_yS_z$ with $3.2 \leq x \leq 3.8$, $0.13 \leq y \leq 0.4$, $0 \leq z \leq 0.2$, $2.9 \leq w \leq 3.3$, or the compounds in the form of $Li_tP_xAl_yO_uN_vS_w$ with $5x + 3y = 5$, $2u + 3v + 2w = 5 + t$, $2.9 \leq t \leq 3.3$, $0.84 \leq x \leq 0.94$, $0.094 \leq y \leq 0.26$, $3.2 \leq u \leq 3.8$, $0.13 \leq v \leq 0.46$, $0 \leq w \leq 0.2$;

- materials based on lithium phosphorus or lithium boron oxynitrides, called respectively “LiPON” and “LIBON”, also able to contain silicon, sulfur, zirconium, aluminum, or a combination of aluminum, boron, sulfur and/or silicon, and boron for materials based on lithium phosphorus oxynitrides;
- lithiated compounds based on lithium silicon phosphorus oxynitride called “LiSiPON”, and in particular $Li_{1.9}Si_{0.28}P_{1.0}O_{1.1}N_{1.0}$;
- lithium oxynitrides of the LiBON, LiBSO, LiSiPON, LiSON, thio-LiSiCON and LiPONB types (where B, P and S represent respectively boron, phosphorus and sulfur);
- lithium oxides of the LiBSO type such as $(1 - x)LiBO_2 - xLi_2SO_4$ with $0.4 \leq x \leq 0.8$;
- silicates, preferably selected from $Li_2Si_2O_5$, Li_2SiO_3, $Li_2Si_2O_6$, $LiAlSiO_4$, Li_4SiO_4, $LiAlSi_2O_6$;
- solid electrolytes of the anti-perovskite type selected from: Li_3OA with A a halide or a mixture of halides, preferably at least one of the elements selected from F, Cl, Br, I or a mixture of two or three or four of these elements; $Li_{(3-x)}M_{x/2}OA$ with $0 < x \leq 3$, M a divalent metal, preferably at least one of the elements selected from Mg, Ca, Ba, Sr or a mixture of two or three or four of these elements, A a halide or a mixture of halides, preferably at least one of the elements selected from F, Cl, Br, I or a mixture of two or three or four of these elements; $Li_{(3-x)}M^3_{x/3}OA$ with $0 \leq x \leq 3$, M^3 a trivalent metal, A a halide or a mixture of halides, preferably at least one of the elements selected from F, Cl, Br, I or a mixture of two or three or four of these elements; or $LiCOX_zY_{(1-z)}$, with X and Y halides as mentioned above in relation to A, and $0 \leq z \leq 1$.

10. Method for manufacturing an anode located inside a lithium-ion battery, said battery comprising at least one cathode, at least one electrolyte and at least one anode, said anode comprising an anodic member capable of being manufactured by the method according to any one of claims 1 to 9, said method for manufacturing the anode being characterized in that the pores of said porous layer are loaded with metallic lithium during the first charging of the battery.

11. Anodic member for a lithium-ion battery, able to be obtained by the method according to any one of claims 1 to 9.

12. Method for manufacturing a non-charged lithium-ion battery, implementing the method for manufacturing an anodic member according to one of claims 1 to 9 and comprising the steps of:

(1) Preparing an anodic member disposed on a substrate, preferably on a metal substrate, or adhesively bonded to an electrically conductive sheet, said substrate or said electrically conductive sheet being able to serve as a current collector of the battery;

(2) Preparing a cathode on a substrate, which may be a metal substrate that can serve as a current collector of the battery;

(3) Depositing a colloidal suspension of solid electrolyte particles on the anode and/or on the cathode, followed by drying;

(4) Face-to-face stacking of the anodic member and of the cathode, followed by thermopressing.

13. Manufacturing method according to claim 12, comprising the steps:

(i) Providing

- a cathode layer disposed on a substrate, capable of serving as a current collector of the battery, preferably on a metal substrate;
- a colloidal suspension comprising aggregates or agglomerates of monodisperse nanoparticles of at least one first electrically insulating material conducting lithium ions with a mean primary diameter D_{50} of between 5 nm and 100 nm, said aggregates or agglomerates having a mean diameter of less than 500 nm;
- at least one substrate, said substrate being able to be a metal substrate capable of serving as a current collector of said battery or being an intermediate substrate;
- when an intermediate substrate is provided, providing
  - at least one electrically conductive sheet able to serve as a current collector of the battery;
  - a conductive glue or a colloidal suspension comprising monodisperse nanoparticles of at least one second material conducting lithium ions with a mean primary diameter D_{50} of between 5 nm and 100 nm;

(ii) Depositing at least one porous layer, by electrophoresis, by the inkjet printing method, by doctor blade, by spraying, by flexographic printing, by roller coating, by curtain coating or by dip coating, using said colloidal suspension comprising aggregates or agglomerates of monodisperse nanoparticles of the at least one first material conducting lithium ions on said substrate and/or on said cathode layer;

(iii) Drying the layer thus obtained at step (ii), where applicable before or after having separated the layer from its intermediate substrate, optionally followed by heat treatment, preferably under oxidizing atmosphere, of the dried layer obtained,

a. and, when the intermediate substrate is used, depositing on at least one face, preferably on both faces, of said electrically conductive sheet, a thin layer of

conductive glue or a thin layer of nanoparticles using the colloidal suspension comprising monodisperse nanoparticles of at least a second material conducting lithium ions, the second material conducting the lithium ions preferably being identical to the first material conducting lithium ions;

b. followed by the adhesive bonding of the porous layer on said face, preferably on both faces of said electrically conductive sheet;

(iv) Optionally, depositing, by the atomic layer deposition ALD technique, a layer of a lithiophilic material on and inside the pores of the porous layer obtained at step (iii);

(v) Optionally, depositing a layer of solid electrolyte on the cathode layer and/or on the porous layer obtained at step (iii) and/or step (iv), said layer of solid electrolyte being obtained from an electrolyte material having an electron conductivity of less than 10^{-10} S/cm, preferably less than 10^{-11} S/cm, electrochemically stable in contact with metallic lithium and at the operating potential of the cathodes, having an ion conductivity greater than 10^{-6} S/cm, preferentially greater than 10^{-5} S/cm;

(vi) Drying the layer thus obtained at step (v);

(vii) Producing a stack comprising an alternating succession of cathode and porous layers, preferably offset laterally;

(viii) Hot pressing the stack obtained at step (vii) so as to juxtapose the films obtained at step (v) present on the anode and cathode layers, and so as to obtain an assembled stack.

14. Method according to claim 12 or 13, wherein the step of depositing a layer of solid electrolyte is implemented using a suspension of core-shell nanoparticles comprising particles of a material that can serve as electrolyte, on which a polymer shell is grafted, preferably selected from the group formed by polyethylene oxide, abbreviated to PEO, polypropylene oxide, abbreviated to PPO, polydimethylsiloxane, abbreviated to PDMS, polyacrylonitrile PAN, polymethyl methylmethacrylate, abbreviated to PMMA, polyvinyl chloride, abbreviated to PVC, polyvinylidene difluoride, abbreviated to PVDF, polyvinylidene fluoride-co-hexafluoropropylene, and polyacrylic acid, abbreviated to PAA.

15. Method according to claim 14, wherein the shell polymer of the core-shell nanoparticles is a grafted polymer including ion groups having lithium ions or OH groups the hydrogen of which has at least partly, preferably totally, been substituted by lithium.

16. Method for manufacturing a non-charged, according to any one of claims 12 to 15, wherein, after the last step, there are deposited successively, in alternation, on the assembled stack, an encapsulation system that comprises a first layer of polymer, followed

by a second inorganic insulating layer, this sequence being able to be repeated several times, on the understanding that said polymer layer can be selected in particular from parylene, type F parylene, polyimide, epoxy resins, polyamide and a mixture thereof, and said inorganic layer can be selected in particular from ceramics, glasses, vitroceramics, which are advantageously deposited by ALD or HDPCVD.

17. Method for manufacturing a charged battery, implementing the method for manufacturing a non-charged battery according to any one of claims 12 to 16, comprising an additional step of loading the pores of the porous layer with metallic lithium during the first charging of the non-charged battery

18. Anode able to be obtained by the method according to claim 10, said anode comprising a porous layer, having a porosity of between 35% and 70% by volume, and preferably between 35% and 55% by volume, deposited on a metal substrate, and metallic lithium loaded inside the pores of the porous layer, said anode being located inside a lithium-ion battery.

19. Non-charged lithium-ion battery, comprising at least one anodic member according to claim 11.

20. Lithium-ion battery, characterized in that it comprises at least one anode according to claim 18, preferably with an anode thickness greater than 20 μm.

21. Lithium-ion battery according to one of claims 19 or 20, characterized in that it comprises a solid electrolyte consisting of nanoparticles of a conductor of lithium ions, which may be of the NASICON type, said nanoparticles being coated with a polymer phase with a thickness of less than 150 nm, preferably less than 100 nm and even more preferentially less than 50 nm, said polymer phase preferably being selected from the group formed by polyethylene oxide, abbreviated to PEO, polypropylene oxide, abbreviated to PPO, polydimethylsiloxane, abbreviated to PDMS, polyacrylonitrile PAN, polymethyl methylmethacrylate, abbreviated to PMMA, polyvinylchloride, abbreviated to PVC, polyvinylidene fluoride, abbreviated to PVDF, polyvinylidene fluoride-co-hexafluoropropylene, polyacrylic acid, abbreviated to PAA; the thickness of this solid electrolyte is preferably less than 20 μm.

22. Lithium-ion battery according to any one of claims 19 to 21, characterized in that it comprises a cathode including a continuous mesoporous lattice made from mesoporous lithiated oxide, coated with a nanolayer of an electron-conducting material such as carbon, the mesoporosity of this cathode preferably being between 25% and 50% by volume, and said cathode being filled with a phase conducting lithium ions.