CLAIMS

1. A porous anode for a lithium-ion battery, including at least one anode material and being binder-free, said anode being precharged with lithium ions, characterized in that said anode material, deposited on an electronic conductor substrate capable of serving as anode current collector, is coated with a protective coating in contact with said anode material, said protective coating being capable of protecting said anode material from the atmosphere of the environment; wherein said anode material has a porosity greater than 30% by volume.

2. The porous anode according to claim 1, characterized in that said anode can be manufactured by a chemical vapor deposition technique, in particular by a physical vapor deposition technique such as cathode sputtering, and/or by a chemical vapor deposition technique, possibly plasma assisted.

3. The porous anode according to claim 1, characterized in that said anode can be manufactured by an electrophoretic deposition technique from a suspension of nanoparticles of at least one anode material.

4. The porous anode according to any of claims 1 to 3, characterized in that said anode material is chosen from the group formed by:

   - carbon nanotubes, graphene, graphite;
   - lithium iron phosphate, of typical formula $LiFePO_4$;
   - mixed silicon and tin oxinitrides, of typical formula $Si_aSn_bO_yN_z$ with $a>0$, $b>0$, $a+b\leq 2$, $0<y\leq 4$, $0<z\leq 3$, also called SiTON, and in particular $SiSn_{0.87}O_{1.2}N_{1.72}$;
   - oxynitride carbides of typical formula $Si_aSn_bC_cO_yN_z$ with $a>0$, $b>0$, $a+b\leq 2$, $0<c<10$, $0<y<24$, $0<z<17$;
   - nitrides of the type Si_xN_y, in particular with $x=3$ and $y=4$; of type Sn_xN_y, in particular with $x=3$ and $y=4$; of type Zn_xN_y, in particular with $x=3$ and $y=2$; of type $Li_{3-x}M_xN$ with $0\leq x\leq 0.5$ for M=Co, $0\leq x\leq 0.6$ for M=Ni, and $0\leq x\leq 0.3$ for M=Cu; or of type $Si_{3-x}M_xN_4$ with $0\leq x\leq 3$;
   - 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.

5. The porous anode according to any of claims 3 or 4, characterized in that it is porous, preferably mesoporous.

6. The porous anode according to any of claims 1 to 5, characterized in that said protective coating comprises a first layer, in contact with the anode material, deposited by the ALD technique (Atomic Layer Deposition) or chemically in a solution CSD, which has a thickness less than 10 nm, preferably less than 5 nm, and that is even more preferably comprised between 1 nm and 3 nm.

7. The porous anode according to claim 6, characterized in that said this first layer is an electronic insulator oxide, preferably selected from the group formed by silica, alumina and zirconia.

8. The porous anode according to any of claims 6 to 7, characterized in that said protective coating comprises a second layer, deposited on top of the first layer, that is made of a material selected from the group formed by:

- phosphates such as Li_3PO_4, $LiPO_3$, $(Li_3Al_{0.4}Sc_{1.6}(PO_4)_3$, $Li_{1.2}Zr_{1.9}Ca_{0.1}(PO_4)_3$; $LiZr_2(PO_4)_3$; $Li_{1+3x}Zr_2(P_{1-x}Si_xO_4)_3$ 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 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 mixture of the two compounds and $0 \leq x \leq 0.8$; $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ with $0 \leq x \leq 1$, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO4)_3$, or $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ with $0 \leq x \leq 1$; 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 $0 \leq y \leq 1.0$ & $0 \leq z \leq 0.6$ and M= Al, Ga or Y or a mixture of two or three of these compounds; $Li_{3+y}(Sc_{2-x}M_x)Q_yP_{3-y}O_{12}$, 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 $Li_{1+x}N_xM_{2-x}P_3O_{12}$, with $0 \leq x \leq 1$ and N= Cr, V, Ca, B, Mg, Bi and/or Mo, M = Sc, Sn, Zr, Hf, Se or Si, or a mixture of these compounds;
- borates such as Li_3BO_3, $LiBO_2$, $Li_3(Sc_{2-x}M_x)(BO_3)_3$ with M=Al or Y and $0 \leq x \leq 1$; $Li_{1+x}M_x(Sc)_{2-x}(BO_3)_3$ with $0 \leq x \leq 0.8$ and M = Al, Y, Ga or a mixture of the three compounds; $Li_{1+x}M_x(Ga_{1-y}Sc_y)_{2-x}(BO_3)_3$ 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_2SO_4, Li_3BO_3-Li_2SiO_4, Li_3BO_3-Li_2SiO_4-Li_2SO_4;

- silicates such as Li_2SiO_3, $Li_2Si_5O_{11}$, $Li_2Si_2O_5$, Li_2SiO_6, $LiAlSiO_4$, Li_4SiO_4, $LiAlSi_2O_6$;
- oxides such as a coating of Al_2O_3, $LiNbO_3$;
- fluorides such as AlF_3, LaF_3, CaF_2, LiF, CeF_3;
- compounds of the anti-perovskite type chosen from: Li_3OA with A a halide or a mixture of halides, preferably at least one of the elements chosen 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 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 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 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 such as mentioned hereinabove in relation with A, and $0 \leq z \leq 1$,
- a mixture of different compositions contained in said group.

9. The porous anode according to any of claims 1 to 5, characterized in that said protective coating comprises at least one compound chosen from the group formed by:

   - garnets, preferably chosen from: $Li_7La_3Zr_2O_{12}$; $Li_6La_2BaTa_2O_{12}$; $Li_{5.5}La_3Nb_{1.75}In_{0.25}O_{12}$; $Li_5La_3M_2O_{12}$ with M = Nb or Ta or a mixture of the two compounds; $Li_{7-x}Ba_xLa_{3-x}M_2O_{12}$ with $0 \leq x \leq 1$ and M = Nb or Ta or a mixture of the two compounds; $Li_{7-x}La_3Zr_{2-x}M_xO_{12}$ with $0 \leq x \leq 2$ and M = Al, Ga or Ta or a mixture of two or three of these compounds;
   - lithium phosphates, preferably chosen from: Li_3PO_4; $LiPO_3$; $Li_3Al_{0.4}Sc_{1.6}(PO_4)_3$ under the acronym LASP, $Li_{1.2}Zr_{1.9}Ca_{0.1}(PO_4)_3$; $LiZr_2(PO_4)_3$; $Li_{1+3x}Zr_2(P_{1-x}Si_xO_4)_3$ 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 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 mixture of the two compounds and $0 \leq x \leq 0.8$; $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ with $0 \leq x \leq 1$, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO4)_3$, or $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ with $0 \leq x \leq 1$; 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 $0 \leq y \leq 1.0$ & $0 \leq z \leq 0.6$ and M= Al, Ga or Y or a mixture of two or three of these compounds; $Li_{3+y}(Sc_{2-x}M_x)Q_yP_{3-y}O_{12}$, 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 $Li_{1+x}N_xM_{2-x}P_3O_{12}$, with $0 \leq x \leq 1$ and N= Cr, V, Ca, B, Mg, Bi and/or Mo, M = Sc, Sn, Zr, Hf, Se or Si, or a mixture of these compounds;

- lithium borates, preferably chosen from: $Li_3(Sc_{2-x}M_x)(BO_3)_3$ with M=Al 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 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, $LiBO_2$, Li_3BO_3-Li_2SO_4, Li_3BO_3-Li_2SiO_4, Li_3BO_3-Li_2SiO_4-Li_2SO_4;
- oxinitrides, preferably chosen from $Li_3PO_{4-x}N_{2x/3}$, $Li_4SiO_{4-x}N_{2x/3}$, $Li_4GeO_{4-x}N_{2x/3}$ with $0 < x < 4$ or $Li_3BO_{3-x}N_{2x/3}$ with $0 < x < 3$;
- lithium compounds based on lithium and phosphorus oxinitride (called LiPON) in the form $Li_xPO_yN_z$ 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 boron oxinitrides (called LiPON and LIBON) also able to contain silicon, sulfur, zirconium, aluminum, or a combination of aluminum, boron, sulfur and/or silicon, and boron for the materials based on lithium phosphorus oxinitrides;
- lithium compounds based on lithium, phosphorus and silicon oxinitride called LiSiPON, and particularly $Li_{1.9}Si_{0.28}P_{1.0}O_{1.1}N_{1.0}$;
- lithium oxinitrides of the LiBON, LiBSO, LiSiPON, LiSON, thio-LiSiCON, LiPONB types (where B, P and S represent boron, phosphorus and sulfur respectively);
- lithium oxides, preferably chosen from $Li_7La_3Zr_2O_{12}$ or $Li_{5+x}La_3(Zr_x,A_{2-x})O_{12}$ with A=Sc, Y, Al, Ga and $1.4 \leq x \leq 2$ or $Li_{0.35}La_{0.55}TiO_3$ or $Li_{3x}La_{2/3-x}TiO_3$ with $0 \leq x \leq 0.16$;
- silicates, preferably chosen from $Li_2Si_2O_5$, Li_2SiO_3, Li_2SiO_6, $Li_2Si_2O_6$, $LiAlSiO_4$, Li_4SiO_4, $LiAlSi_2O_6$, $Li_2Si_5O_{11}$;
- solid electrolytes of the anti-perovskite type chosen from: Li_3OA with A a halide or a mixture of halides, preferably at least one of the elements chosen 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 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 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 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 such as mentioned hereinabove in relation with A, and $0 \leq z \leq 1$,

- the compounds $La_{0.51}Li_{0.34}Ti_{2.94}$, $Li_{3.4}V_{0.4}Ge_{0.6}O_4$, Li_2O-Nb_2O_5, $LiAlGaSPO_4$;
- formulations based on Li_2CO_3, B_2O_3, Li_2O, $Al(PO_3)_3LiF$, P_2S_3, Li_2S, Li_3N, $Li_{14}Zn(GeO_4)_4$, $Li_{3.6}Ge_{0.6}V_{0.4}O_4$, $LiTi_2(PO_4)_3$, $Li_{3.25}Ge_{0.25}P_{0.25}S_4$, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$, $Li_{1+x}Al_xM_{2-x}(PO_4)_3$ (where M = Ge, Ti, and/or Hf, and where $0 < x < 1$), $Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$ (where $0 \leq x \leq 1$ and $0 \leq y \leq 1$), $LiNbO_3$.

10. A method for manufacturing a porous anode for a lithium-ion battery according to one of claims 1 to 9, comprising the steps of:

    (a) Deposition of an anode material on said substrate;
    (b) Deposition of a protective coating on said anode material;
    (c) Charging said anode material with lithium ions by polarization in a solution containing lithium cations.

11. The method according to claim 10, wherein the deposition of said anode material is done by a chemical vapor deposition technique, in particular by a physical vapor deposition technique such as cathode sputtering, and/or by a chemical vapor deposition technique, possibly plasma assisted.

12. The method according to claim 10, wherein the deposition of said anode material is done by electrophoresis from a suspension of nanoparticles of at least one anode material, or by dipping.

13. The method according to claim 12, wherein said suspension comprises nanoparticles of at least one anode material with a primary diameter D_{50} less than or equal to 50 nm.

14. The method according to claim 12, wherein said suspension includes aggregates of nanoparticles of anode material.

15. The method according to any of claims 12 to 14, characterized in that said anode material is subjected to a drying, said drying taking place between the end of the deposition by electrophoresis and the beginning of the deposition of the protective coating.

16. The method according to claim 15, characterized in that said anode material is subjected after drying to an annealing, possibly preceded and/or accompanied by a pressing.

17. The method according to any of claims 10 to 16, characterized in that said anode material is chosen from the group formed by:

- carbon nanotubes, graphene, graphite;
- lithium iron phosphate, of typical formula $LiFePO_4$;
- mixed 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 $SiSn_{0.87}O_{1.2}N_{1.72}$;
- 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; of type Sn_xN_y, in particular with x=3 and y=4; of type Zn_xN_y, in particular with x=3 and y=2; of type $Li_{3-x}M_xN$ with 0≤x≤0.5 for M=Co, 0≤x≤0.6 for M=Ni, and 0≤x≤0.3 for M=Cu; or of type $Si_{3-x}M_xN_4$ with 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.

18. The method according to any of claims 10 to 17, wherein the deposition of the protective coating comprises the deposition by ALD or chemically in a solution of a layer of an electronically insulating material, preferably selected from alumina, silica or zirconia, or from a lithium-ion-conducting solid electrolyte material, preferably Li_3PO_4, said protective coating having a thickness comprised between 1 nm and 5 nm, and preferably between 2 nm and 4 nm.

19. The method according to claim 18, wherein after the deposition by ALD or chemically in a solution of a layer of an electronically insulating material or of a solid electrolyte, is carried out a deposition of a thin layer of at least one solid electrolyte by dipping or by electrophoresis is carried out from a suspension including monodispersed nanoparticles of at least one solid electrolyte material.

20. A lithium-ion battery, including a porous anode according to one of claims 1 to 9, or including an anode that can be obtained by the method according to one of claims

10 to 19, and furthermore including an electrolyte in contact with said anode, and a cathode in contact with said electrolyte.

21. The battery according to claim 20, characterized in that said electrolyte is a conductor of lithium ions and is selected from the group formed by:

- all-solid-state electrolytes deposited by vapor phase deposition,
- all-solid-state electrolytes electrophoretically deposited,
- the electrolytes formed by a separator impregnated with a liquid electrolyte, typically with an aprotic solvent comprising a lithium salt or ionic liquid containing one or more lithium salts or a mixture of the two,
- the porous electrolytes, preferably mesoporous impregnated with a liquid electrolyte, typically with an aprotic solvent comprising a lithium salt or ionic liquid containing one or more lithium salts or a mixture of the two,
- the electrolytes comprising a polymer impregnated with a liquid electrolyte and/or a lithium salt,
- the electrolytes formed by a lithium-ion-conducting solid electrolyte material, and preferably one oxide, sulfide or phosphate.

22. The battery according to claim 20 or 21, characterized in that said cathode is an all-solid-state cathode or a porous cathode, preferably mesoporous.