CLAIMS

1. A ~~Thin~~thin-layer electrolyte (13, 23) in an electrochemical device such as a lithium-ion battery, said electrolyte comprising a porous inorganic layer impregnated with a phase carrying lithium ions, characterized in that:

- said porous inorganic layer has an interconnected network of open pores; and

- the open pores of said porous inorganic layer have an average diameter D_{50} less than 100 nm, preferably less than 80 nm, preferably comprised between 2 nm and 80 nm, and more preferably comprised between 2 nm and 50 nm, and a volume greater than 25% of the total volume of said thin-layer electrolyte, and preferably greater than 30%.

~~2. Thin-layer electrolyte (13, 23) according to claim 1, characterized in that the open pores of said porous inorganic layer have an average diameter D_{50} less than 100 nm, preferably less than 80 nm, preferably comprised between 2 nm and 80 nm, and more preferably comprised between 2 nm and 50 nm, and volume greater than 25% of the total volume of said thin-layer electrolyte, and preferably greater than 30%.~~

~~3~~2. The ~~Thin~~thin-layer electrolyte (13, 23) according to claim 1 ~~or claim 2~~, characterized in that the open pores of said porous inorganic layer have a volume comprised between 30% and 50% of the total volume of said thin-layer electrolyte.

~~4~~3. The ~~Thin~~thin-layer electrolyte (13, 23) according to ~~any of claims 1 to 3~~claim 1 or 2, characterized in that said porous inorganic layer is organic binder-free.

~~5~~4. The ~~Thin~~thin-layer electrolyte (13, 23) according to any of claims 1 to ~~4~~3, characterized in that the thickness thereof is less than 10 µm, preferably comprised between 3 µm and 6 µm, and preferably comprised between 2.5 µm and 4.5 µm.

~~6~~5. The ~~Thin~~thin-layer electrolyte (13, 23) according to any of claims 1 to ~~5~~4, characterized in that said porous inorganic layer comprises an electronically-insulating material, preferably chosen from Al_2O_3, SiO_2, ZrO_2, and/or a material selected in the group formed by:

- garnets of formula $Li_d A^1_x A2_y(TO_4)_z$ where

- A^1 represents a cation of oxidation state +II, preferably Ca, Mg, Sr, Ba, Fe, Mn, Zn, Y, Gd; and where
- A^2 represents a cation of oxidation state +III, preferably Al, Fe, Cr, Ga, Ti, La; and where
- (TO_4) represents an anion wherein T is an atom of oxidation state +IV, located at the center of a tetrahedron formed by the oxygen atoms, and wherein TO_4 advantageously represents the silicate or zirconate anion, knowing that all or a portion of the elements T of an oxidation state +IV can be replaced by atoms of an oxidation state +III or +V, such as Al, Fe, As, V, Nb, In, Ta;
- knowing that: d is comprised between 2 and 10, preferably between 3 and 9, and more preferably between 4 and 8; x is comprised between 2.6 and 3.4 (preferably between 2.8 and 3.2); y is comprised between 1.7 and 2.3 (preferably between 1.9 and 2.1) and z is comprised between 2.9 and 3.1;

o 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;

o lithium phosphates, preferably chosen from: lithium phosphates of the NaSICON type, Li_3PO_4; $LiPO_3$; $Li_3Al_0{,}4Sc_{1.6}(PO_4)_3$ called "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 $0 \leq x \leq 1$ called "LATP"; or $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ with $0 \leq x \leq 1$ called "LAGP"; or $Li_{1+x+z}Mx(Ge_{1-y}Ti_y)_{2-x}Si_zP_{3-z}O_{12}$ 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; $Li_{3+y}(Sc_{2-x}Mx)Q_yP_{3-y}O_{12}$, 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 $Li_{1+x+y}MxSc_{2-x}Q_yP_{3-y}O_{12}$, 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 $Li_{1+x+y+z}Mx(_{Ga1-y}Sc_y)_{2-x}Q_zP_{3-z}O_{12}$ 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;

- 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, 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 oxinitride and phosphorus, called "LiPON", in the form LixPOyNz with x ~2.8 and 2y+3z ~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, respectively 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 oxinitrides of the LiBSO type such as $(1-x)LiBO_2$ - xLi_2SO_4 with $0.4 \leq x \leq 0.8$;
- 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 Li3xLa$_{2/3-x}$TiO$_3$ with $0 \leq x \leq 0.16$ (LLTO);
- silicates, preferably chosen 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 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 $0 \leq z \leq 1$,

- o 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, $LiAlGaSPO_4$;
- o 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 $0 \leq y \leq 1$).

~~7~~6. The ~~Thin~~thin-layer electrolyte (13, 23) according to any of claims 1 to ~~6~~5, characterized in that said pores are impregnated with a phase carrying lithium ions, such an organic solvent or a mixture of solvents wherein at least one lithium salt is dissolved, and/or a polymer containing at least one lithium salt, and/or an ionic liquid or a mixture of ionic liquids, possibly diluted with a suitable solvent, containing at least one lithium salt.

~~8~~7. The ~~Thin~~thin-layer electrolyte (13, 23) according to any of claims 1 to ~~6~~5, 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.

~~9~~8. A ~~Method~~ method for manufacturing a thin-layer electrolyte (13, 23) deposited on an electrode (12, 22), said layer being preferably free of organic binder and preferably having a porosity, preferably mesoporous, greater than 30% by volume, and more preferably comprised between 30% and 50% by volume, and said layer having pores with an average diameter D_{50} less than 100 nm, preferably less than 80 nm and preferably 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 inorganic material, said aggregates or agglomerates having an average diameter comprised between 80 nm and 300 nm (preferably between 100 nm to 200 nm),

(b) an electrode (12, 22) is provided,

(c) a porous inorganic layer is deposited on said electrode by electrophoresis, by ink-jet, by doctor blade, by roll coating, by curtain coating or by dip-coating, from a suspension of particles of inorganic material obtained in step (a);

(d) said porous inorganic layer is dried, preferably in an airflow to obtain a porous inorganic layer;

(e) said porous inorganic layer is treated by mechanical compression and/or heat treatment,

(f) said porous inorganic layer obtained in step € is impregnated with a phase carrying lithium ions.

~~10~~9. A ~~Method~~ method for manufacturing a thin-layer electrolyte (13, 23) deposited on an electrode, said layer being preferably free of organic binder and preferably having a porosity, preferably mesoporous, greater than 30% by volume, and more preferably comprised between 30% and 50% by volume, and said layer having pores with an average diameter D_{50} less than 100 nm, preferably less than 80 nm, preferably less than 50 nm, said method being characterized in that:

(a1) a colloidal suspension is provided including nanoparticles of at least one inorganic material P with a primary diameter D_{50} 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) an electrode is provided;

(c) a porous inorganic layer is deposited on said electrode 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 particles of at least one inorganic material obtained in step (a2);

(d) the porous inorganic layer is dried, preferably in an airflow to obtain a porous inorganic layer;

(e) said porous inorganic layer is treated by mechanical compression and/or heat treatment,

(f) said porous inorganic layer obtained in step (e) is impregnated with a phase carrying lithium ions.

~~11~~10. The ~~Method~~ method according to claims ~~9~~ 8 or ~~10~~9, wherein the porous inorganic layer obtained in step (c) has a thickness less than 10 µm, preferably less than 8 µm, and more preferably comprised between 1 µm and 6 µm.

~~12~~11. The ~~Method~~ method according to any of claims ~~9~~ 8 to ~~11~~10, wherein the porous inorganic layer obtained in step (d) has a thickness less than 10 µm, preferably comprised between 3 µm and 6 µm, and preferably comprised between 2.5 µm and 4.5 µm.

~~13~~12. The ~~Method~~ method according to any of claims ~~9~~ 8 to ~~12~~11, wherein the primary diameter of said nanoparticles is comprised between 10 nm and 50 nm, preferably between 10 nm and 30 nm.

~~14~~13. The ~~Method~~ method according to any of claims ~~9~~ 8 to ~~13~~12, wherein the average diameter of the pores is comprised between 2 nm and 50 nm, preferably comprised between 6 nm and 30 nm and more preferably between 8 nm and 20 nm.

~~15~~14. The ~~Method~~ method according to any of claims ~~9~~ 8 to ~~14~~13, wherein the electrode is a dense electrode or a porous electrode, preferably a mesoporous electrode.

~~16~~15. Use of a process according to any one of claims ~~9~~ 8 to ~~15~~ 14 for the manufacture of thin-layer electrolytes, preferably in a thin layer, in electronic, electrical or electrotechnical devices and preferably in devices selected in the group composed of batteries, capacitors, supercapacitors, capacities, resistors, inductors, transistors.

~~17~~16. A ~~Process~~ process for manufacturing a thin-layer battery, implementing the method according to any of claims ~~9~~ 8 to ~~15~~14, and comprising the steps of:

-1- providing at least two conductive substrates (11, 21) covered beforehand with a layer of material that can be used as an anode and, respectively, as a cathode ("anode layer" respectively "cathode layer"),

-2- providing a colloidal suspension, containing aggregates or agglomerates of nanoparticles of at least one inorganic material, said aggregates or said agglomerates having an average diameter comprised between 80 nm and 300 nm (preferably between 100 nm to 200 nm),

-3- Deposition of a porous inorganic layer by electrophoresis, by ink-jet, by doctor blade, by roll coating, by curtain coating or by dip-coating, from a suspension of aggregated particles of inorganic material obtained in step -2- on the cathode, respectively anode layer, obtained in step -1-,

-4- Drying of the layer thus obtained in step -3-, preferably in an air flow,

-5- Stacking of layers of cathode and anode, preferably offset laterally,

-6- Treating the stack of anode and cathode layers obtained in step -5- by mechanical compression and/or heat treatment so as to juxtapose and assemble the porous inorganic layers present on the anode and cathode layers,

-7- Impregnating of the structure obtained in step -6- with a phase carrying lithium ions, preferably with a phase carrying lithium ions comprising at least 50% by weight of at least one ionic liquid leading to the obtaining of an assembled stack, preferably a battery.

~~18~~17. The process~~Method~~ according to claim ~~17~~16, wherein the cathode is a dense electrode

or a dense electrode coated by ALD with an electronically-insulating layer, preferably an electronically insulating and ionic conducting layer,

or a porous electrode,

or a porous electrode coated by ALD with an electronically-insulating layer, preferably an electronically insulating and ionic conducting layer,

or, preferably, a mesoporous electrode, or a mesoporous electrode coated by ALD with an electronically-insulating layer, preferably an electronically insulating and ionic conducting layer,

and/or wherein the anode is a dense electrode,

or a dense electrode coated by ALD with an electronically-insulating layer, preferably an electronically insulating and ionic conducting layer,

or a porous electrode,

or a porous electrode coated by ALD with an electronically-insulating layer, preferably an electronically insulating and ionic conducting layer,

or, preferably, a mesoporous electrode,

or a mesoporous electrode coated by ALD with an electronically-insulating layer, preferably an electronically insulating and ionic conducting layer.

~~19~~18. The process~~Method~~ according to any of claims ~~17~~ 16 to ~~18~~17, wherein after step -7-:

- is deposited successively, alternating, on the battery:
  - at least one first layer of parylene and/or polymide on said battery,
  - at least one second layer composed of an electrically-insulating material by ALD (Atomic Layer Deposition) on said first layer of parylene and or polyimide,
  - and on the alternating succession of at least one first and of at least one second layer is deposited a layer making it possible to protect the battery from mechanical damage of the battery, preferably made of silicone, epoxy resin, or parylene or polyimide, thus forming, an encapsulation system of the battery,
- the battery thus encapsulated is cut along two cutting planes to expose on each one of the cutting plans anode and cathode connections of the battery, in such a way that the encapsulation system covers four of the six faces of said battery, preferably continuously,
- is deposited successively, on and around, these anode and cathode connections:
  - optionally, a first electronically-conductive layer, preferably metallic, preferably deposited by ALD,
  - a second layer with an epoxy resin base charged with silver, deposited on the first electronically-conductive layer, and
  - a third layer with a nickel base, deposited on the second layer, and
  - a fourth layer with a tin or copper base, deposited on the third layer.

~~20~~19. The process~~Method~~ according to claim ~~17~~16, wherein after step -6-:

- is deposited successively, alternating, on the assembled stack, an encapsulation system (30) 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 naphthalate (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 (7),

- is deposited successively, on and around, these anode and cathode connections (50):
    - 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 (50) by a layer of metal copper,
- possibly, is deposited successively, on and around, this first stack of terminations, a second stack comprising:
    - 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 the second stack.

~~21~~20. The process~~Method~~ according to claim ~~20~~19, wherein the anode and cathode connections are on the opposite sides of the stack.

~~22~~21. An ~~Electrochemical~~ electrochemical device comprising at least one thin electrolyte layer according to any of claims 1 or 7, preferably a lithium-ion battery or a supercapacitor.