



(22) Date de dépôt/Filing Date: 1999/05/10

(41) Mise à la disp. pub./Open to Public Insp.: 2000/11/10

(45) Date de délivrance/Issue Date: 2013/07/16

(51) Cl.Int./Int.Cl. *H01M 4/136* (2010.01),
G02F 1/155 (2006.01), *H01G 11/50* (2013.01),
H01M 10/0525 (2010.01), *H01M 4/58* (2010.01),
H01M 4/06 (2006.01), *H01M 4/62* (2006.01)

(72) Inventeurs/Inventors:
ARMAND, MICHEL, CA;
MICHOT, CHRISTOPHE, FR;
RAVET, NATHALIE, CA;
SIMONEAU, MARTIN, CA;
HOVINGTON, PIERRE, CA

(73) Propriétaires/Owners:
HYDRO-QUEBEC, CA;
UNIVERSITE DE MONTREAL, CA;

(54) Titre : MATERIAUX D'ELECTRODES A INSERTION DE LITHIUM A BASE DE DERIVES D'ORTHOSILICATE

(54) Title: LITHIUM INSERTION ELECTRODE MATERIALS BASED ON ORTHOSILICATE DERIVATIVES

(57) Abrégé/Abstract:

There is provided a lithium ion reversible insertion-type electrode material based on orthosilicate structure having the general formula:



There is also provided an electrical generator and a variable optical transmission device comprising the lithium ion reversible insertion-type electrode material as defined above.



(73) **Propriétaires(suite)/Owners(continued):**CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE, FR

(74) **Agent:** NORTON ROSE FULBRIGHT CANADA LLP/S.E.N.C.R.L., S.R.L.

ABSTRACT

There is provided a lithium ion reversible insertion-type electrode material based on orthosilicate structure having the general formula:



There is also provided an electrical generator and a variable optical transmission device comprising the lithium ion reversible insertion-type electrode material as defined above.

TITLE

Lithium insertion electrode materials based on orthosilicate derivatives

FIELD OF THE INVENTION

5 The invention relates to new lithium insertion electrode materials based on orthosilicates derivatives, electrochemical generators and variable optical transmission devices having an electrode containing these materials.

BACKGROUND OF THE INVENTION

10 Electrode materials are mainly derivatives of transition metals chalcogenides, especially oxides having a lemellar structure like Li_xCoO_2 or spinels like $\text{Li}_{2x}\text{Mn}_2\text{O}_4$. These materials usually operate via a lithium insertion mechanism with less than one lithium and electron exchanged per transition metal in the unit formula ($0 \leq X \leq 0.6$). Besides, these materials suffer from facile loss of the transition metal which is leached
15 into the electrolyte. Cobalt is prohibitively expensive for large scale application.

Materials with the olivine structure LiFePO_4 (triphylite) and the quasi-isomorphous delithiated material noted as " $\blacksquare\text{FePO}_4$ " where " $\blacksquare$ " represents the lithium site vacancies, have the advantage of an operating voltage of 3.5 V vs $\text{Li}^+ / \text{Li}^\circ$, i.e. in the
20 stability window of both liquid and polymer electrolytes with a flat discharge (lithium intercalation) plateau. The materials are however limited by relatively both slow Li^+ diffusion kinetics and low electronic conductivity due to the high electronegativity of the phosphate anion. The absence of non-stoichiometry or mutual miscibility for both phases (LiFePO_4 and $\blacksquare\text{FePO}_4$) is an advantage in terms of the shape of the discharge curve but

- 2 -

limits the kinetics of phase transformation which may lead ultimately at high current densities to fragmentation of the material and loss of contact with the carbon grains acting as current collector. The phosphate of this type offers the possibility of exchanging only one lithium per unit formula.

5

Conversely, it is known that the compounds with either the Li_2SO_4 , Li_3PO_4 , Li_4SiO_4 and their solid solutions possess relatively high diffusion coefficients for lithium ions, but have no redox activity.

10 SUMMARY OF THE INVENTION

In the present invention, orthosilicates containing the SiO_4^{4-} tetranion as the building block are used as redox materials by incorporation of at least one transition elements with at least two valency levels. Lithium ingress or egress from the structure to compensate for the valency change of the redox couples during electrode operation and

15 keep overall electroneutrality.

DETAILED DESCRIPTION OF THE INVENTION

The general formula of the materials of the invention is:



20 wherein:

M represents Mn^{2+} or Fe^{2+} and mixtures thereof;

D represents a metal in the +2 oxidation state, chosen among: Mg^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} ,

Cu^{2+} , Ti^{2+} , V^{2+} , Ca^{2+} ;

- 3 -

T represents a metal in the +3 oxidation state, chosen among: Al^{3+} , Ti^{3+} , Cr^{3+} , Fe^{3+} , Mn^{3+} , Ga^{3+} , Zn^{3+} , V^{3+} ;

Q represents a metal in the +4 oxidation state, chosen among: Ti^{4+} , Ge^{4+} , Sn^{4+} , V^{4+} ;

R represents a metal in the +5 oxidation state, chosen among: V^{5+} , Nb^{5+} , Ta^{5+} ;

5 all M, D, T, Q, R, are elements residing in octahedral or tetrahedral sites;

s, p, g, v, a, and b are the stoichiometric coefficient for S^{6+} (sulphate), P^{5+} (phosphate), Ge^{4+} (germanate), V^{5+} (vanadate), Al^{3+} (aluminate), and B^{3+} (borate) respectively residing in the silicon tetrahedral sites.

The stoichiometric coefficients d, t, q, r, p, s, v, a, b are all positive and comprised
10 between zero (inclusive) and 1 (inclusive). Other conditions are:

$$0 \leq x \leq 2; 1 \leq m \leq 2; p + s + v + a + b < 1 \text{ (exclusive);}$$

$$x + 2m + t + 2q + 3r = 4 - p - 2s - v + a + b.$$

Silicon is the second most abundant element in the earth crust, and silicates
15 structures are chemically very robust, and thus electrochemically stable. The preferred transition metals besides iron and manganese are chosen among: titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, niobium and tantalum. The compounds containing a large fraction of iron and/or manganese are preferred due to the abundance and lack of toxicity of these elements. In addition, metals with fixed valency
20 or redox states whose potential lies outside the domain of operation of the electrode can be substituted partially for the transition elements to improve the diffusion characteristics of the lithium ions and/or increase the number of available sites, help control grain size and allow the existence of continuous solid solution between the oxidized and reduced form of the electrode material. These elements are preferably chosen among lithium,

- 4 -

magnesium, calcium, zinc aluminum, gallium and tin. For instance, these substitutions allows for the coexistence of iron and/or manganese in two different oxidation states in the same phase, or introduce specific interactions with other elements having redox levels close to those of Fe and Mn (e.g.: $\text{Fe}^{2+}/\text{Ti}^{4+} \rightleftharpoons \text{Fe}^{3+}/\text{Ti}^{3+}$, $\text{Mn}^{2+}/\text{V}^{5+} \rightleftharpoons \text{Mn}^{3+}/\text{V}^{4+}$ etc.) both of which are favorable to electronic conductivity, while disorder on the anionic site provides preferential diffusion sites for Li^+ .

Another aspect of the invention relates to the possibility to substitute the silicon sites by various elements. The orthosilicate anion being isosteric with the sulfate, phosphate, germanate and vanadate anions, the corresponding elements can easily replace silicon in this type of structure, as does boron and aluminum, offering a wide choice of materials with complete control of the charge density on the anionic sites. Similarly, the propensity of orthosilicates structures to accommodate large fractions of either vacancies or interstitial ions is very favorable to lithium ion diffusion while maintaining the integrity of the structure during lithium intercalation-desintercalation processes.

The materials according to the invention have preferably the orthorombic structures determined by X-ray and electron diffraction for lithium phosphate (a and g forms), both the low and high temperature form, where the metal ions occupy partially either the seven unoccupied tetrahedral sites left or the "stuffed olivine" structure with a partial occupancy of the four octahedral sites (ASTM N° 25-1020 and 15-760) or that of lithium orthosilicate Li_4SiO_4 . Capacities well in excess of 160 mAh/g can be obtained, which are superior than for the conventional electrode materials. Another advantage of the materials of the present invention is to prevent the leaching of transition metals into

- 5 -

the electrolyte due to the high charge of the orthosilicate anion SiO_4^{4-} which binds selectively the multiply charged cations, including the transition elements.

The compounds of the invention are especially useful, when used alone or in admixture with other redox-active compounds, as a component of stable electrode materials in electrochemical cells, and primary or secondary batteries in which the negative electrode is a source of lithium ions. Typical examples include, in a non limiting way, metallic lithium, lithium alloys, nanodispersions of such alloys in a lithium oxide matrix, such as those obtained by reduction of SnO or SnO_2 a lithium intercalation compound in carbon, especially graphite or carbonaceous matters resulting from the pyrolysis of organic derivatives, like petroleum coke or polyparaphenylene, lithium-titanium spinels of general formula $\text{Li}_{1+y}\text{Ti}_{2-x/4}\text{O}_4$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$, 1 independently) and its solid solutions with other spinels, or a lithium-transition metal mixed nitride like, $\text{Li}_{3-x}\text{Co}_x\text{N}$ ($0 \leq x \leq 1$,). These materials can be used alone or in admixtures.

15

Other applications are in supercapacitors or as counter-electrode for controlled reflection-transmission windows ("smart windows") due to the low optical absorption of the compounds in different oxidation states.

20 The compounds of the present invention are easily prepared by the techniques of inorganic chemistry and ceramics known to the man skilled in the art. In general, oxides, salts or derivatives of the elements to be incorporated in the final composition of the material are mixed in a predetermined ratio and heated at a preset temperature to ensure reaction. Preferably, the metallic salts are those derived from anions that easily

- 6 -

decompose at moderate temperatures to leave the oxides. These include the organic salts like acetates, oxalates and in general carboxylic acid derivatives, betadiketonates, alkoxides or mixtures thereof. Preferred inorganic salts similarly are chosen among hydroxides, nitrates, carbonates, sulfates. The so-called sol-gel techniques are especially appreciated as they allow to incorporate the elements in a highly dispersed form which results in homogeneous powders of controllable grain size at relatively low temperature. The silicon alkoxides are especially useful for this purpose as they hydrolyze into silica precursors at room temperature and the silica gel thus formed have a high surface area and adsorbs large quantities of metal salt leading to homogeneous materials upon heat treatment. A wide choice of silicon, titanium, germanium, aluminum derivatives alkoxides are commercially available. Variations of this technique are the coprecipitation of elements from aqueous or non-aqueous media and the Pechini process where polyester-polyacid is formed in solution and chelates the ion from solution this step being followed by drying and pyrolysis. The control of the oxidation level of the elements, especially transition elements can be achieved by working in a controlled environment. Low partial pressures of oxygen can be maintained with vacuum, an inert gas or reducing mixtures like hydrogen or carbon monoxide/carbon dioxide mixture. Well defined oxygen activities can thus be obtained from known thermodynamical data. Conversely, air or oxygen bring the transition element to high valence states.

20

The redox state of the material can also be controlled by chemical extraction or insertion of lithium from the structure, thus mimicking the electrode operation. In a non limiting way, known oxidants able to extract lithium can be chosen among bromine, chlorine, iodine, the nitrosonium or nitronium salts of stable anions like NO^+BF_4^- or

- 7 -

$\text{NO}_2^+\text{PF}_6^-$. Reducing agents, in a non limiting way can be similarly chosen among: the iodide ion, LiBH_4 , the radical-anion derivatives of lithium with condensed aromatic molecules (naphtalene, anthracene, benzophenone), organometallic reagents like butyl lithium, lithium thiolates. The desired degree of lithium content of the compounds of the invention can also be obtained electrochemically.

The following examples are provided to illustrate the present invention and shall by no means be construed as limited its scope.

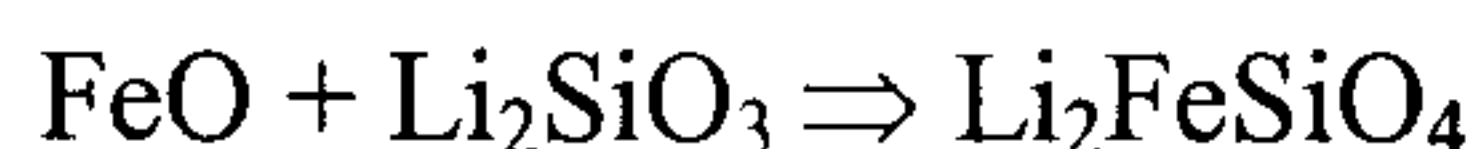
10 EXAMPLES

Example 1

To 90 ml of water and 10 ml of methanol are added 20.4 g of lithium acetate dihydrate $\text{Li}(\text{C}_2\text{H}_3\text{O}_2) \cdot 2(\text{H}_2\text{O})$, 24,5 g of manganese acetate tetrahydrate $(\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4(\text{H}_2\text{O}))$ and 14.8 ml of tetramethoxysilane. The mixture is milled with zirconia pellets in a heavy walled plastic container on a roller mill for 60 hours. The thick slurry is poured onto a PTFE evaporating dish and dried at 90°C in an oven with air circulation. The resulting mass is powdered in a mortar and the organic residues are removed by heat treatment at 350°C in air. The resulting brownish-green powder is transferred to an alumina boat and the compound is treated at 800°C in a electrically heated furnace under a reducing gas stream containing 8% hydrogen diluted in argon. 13 g of $\text{Li}_2\text{MnSiO}_4$ are obtained (81% yield).

Example 2

71.8 g of ferrous oxide FeO and 89.9 of lithium metasilicate Li_2SiO_3 are ball-milled with high carbon steel ball for 4 hours. The resulting mixture is transferred into a quartz ampoule in which some iron turnings are added. The ampoule is evacuated under secondary vacuum while kept at 200°C and sealed. The reaction



is complete at 800°C in 4 hours. After cooling, the ampoule is opened under argon and the iron turnings are removed magnetically.

10 Example 3

Iron protoxide FeO (71.8 g) and lithium metasilicate Li_2SiO_3 (90 g) are ball-milled with high carbon steel ball for 4 hours. The resulting mixture is transferred into a quartz ampoule in which some iron turnings are added. The ampoule is evacuated under secondary vacuum while kept at 200°C and sealed. The reaction



is complete at 800°C in 4 hours.

Example 4

21.6 g of iron oxalate dihydrate, 1.79 g manganese oxalate dihydrate and 5.17 g of lithium carbonate are milled similarly as in example 1 with 13.4 g of polydiethoxysiloxane (Gelest mc, Tullytown PA, USA catalog N° PSI-023) in 100 ml of 96 % ethyl alcohol. The resulting slurry is evaporated and calcined at 500°C under air. The cake is pulverized in a ball mill for 20 minutes and the resulting powder is treated at 1050°C for 10 hours in an tubular furnace under an equivolumic mixture of CO_2 , and CO. The resulting compound has the formula $\text{Li}_{1.4}\text{Fe}_{1.2}\text{Mn}_{0.1}\text{SiO}_4$.

Example 5

To 50 ml of methanol are added 19.4 g of lithium acetate dihydrate $\text{Li}(\text{C}_2\text{H}_3\text{O}_2) \cdot 2(\text{H}_2\text{O})$, 19.6 g of manganese acetate tetrahydrate $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4(\text{H}_2\text{O})$, 14.8 ml of tetramethoxysilane and 2.75 ml of titanium tetraisopropoxide diluted in 20 ml of isopropanol. The mixture is milled with zirconia pellets in a heavy walled plastic container on a roller mill for 60 hours. The slurry is poured onto a PTFE evaporating dish and dried at 80°C in a air circulation oven. The resulting mass is powdered in a mortar and the organic residues are removed by heat treatment at 350°C in air. The resulting powder is transferred to an alumina boat and the compound is treated as in example 1 at 800°C under a reducing gas stream containing 8 % hydrogen diluted in argon. The compound obtained corresponds to the formula $\text{Li}_{1.9}\text{Mn}_{0.8}\text{Ti}_{0.1}\text{SiO}_4$ where Ti is in the +3 state and manganese is divalent.

Example 6

3 g of the compound of example 2, $\text{Li}_2\text{FeSiO}_4$ are suspended in 20 ml of acetonitrile and treated with 1.7 g of bromine under stirring at room temperature. After two hours, the suspension is filtered and washed with acetonitrile leaving a solid having the composition $\text{Li}_1\text{FeSiO}_4$. This corresponds to an electrode capacity of 172 mAh/g. Similarly, 7 g of the material of example 4 are treated with 3 g of bromine in 50 ml of acetonitrile. After filtration, the material $\text{Li}_{0.1}\text{Fe}_{1.2}\text{Mn}_{0.1}\text{SiO}_4$ is obtained. It corresponds to an electrode capacity of 260 mAh/g.

Example 7

- 10 -

5 g of the compound of example 1, $\text{Li}_2\text{MnSiO}_4$ are suspended in 40 ml of nitromethane and treated with 12 g nitronium hexafluorophosphate NO_2PF_6 under stirring at room temperature. After two hours, the suspension is filtered and washed with
5 nitromethane leaving a brownish-purple solid having the composition MnSiO_4 . This corresponds to an electrode capacity of 345 mAh/g.

Example 8

8 g of the compound of example 1, $\text{Li}_2\text{MnSiO}_4$ and 3.36 g of lithium iron phosphate LiFePO_4 are ball-milled with steel balls under an inert atmosphere until the
10 grain size does not exceed 4 microns. The mixture is introduced in a closed-end nickel tube which is evacuated and welded. The tube is treated at 750°C for 10 hours and allowed to cool to room temperature. The solid solution obtained has the formula $\text{Li}_{1.7}\text{Mn}_{0.7}\text{Fe}_{0.3}[\text{Si}_{0.7}\text{P}_{0.3}\text{O}_4]$.

Example 9

15 A solid-state battery using a 10 mm lithium anode laminated on a 10 mm nickel foil, a 25 mm polymer electrolyte and a 45 mm positive electrode is constructed with a total active surface of 4 cm^2 . The electrolyte is a crosslinked condensation polymer prepared according to *J Electrochem. Soc.* 141-7, 1915 (1994) and *Journal of Power Sources*, 54-1, 40 (1995) with lithium trifluoromethane sulfonimide $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$
20 as a solute corresponding to a 16:1 ratio of oxygens from polymer ether groups to Li^+ . The positive electrode is obtained from a slurry of 53% by volume of PEO, molecular weight 200 000, 40 % by volume of the material of example 4 and delithiated according to example 6, and 7% by volume of Ketjenblack® in acetonitrile, by coating technique on

a 12 mm aluminium foil. 1.2 lithium per formula unit can be cycled between 3.5 and 2.4 volts.

Example 10

A gel type rocking-chair ("lithium ion") battery is constructed using a 40 mm
5 anode made from graphite flakes (4 mm) with an ethylene-propylene-diene binder (5%)
by volume, and laminated on a 10 mm copper foil, a 45 mm electrolyte containing a
vinylidene fluoride-hexafluoropropylene copolymer (Solvay, Belgium), 30 ww%, fumed
silica (5 ww%) with gelled with a liquid electrolyte consisting of 1.2 molar lithium
hexafluorophate in equivolumic ethylene carbonate-ethylmethyl carbonate (65 ww%)
10 mixed solvent. The positive electrode consists in a blend of the electrode material of
example 5 (80 ww%), Ketjenblack® (8 ww%) and the vinylidene fluoride-
hexafluoropropylene copolymer used in the electrolyte (12 ww%). The battery is housed
in a flat metal-plastic laminate container allowing for the passage of current leads. At
25°C, the battery operation allows the exchange of 1.3 lithium per manganese in the
15 positive electrode in the voltage range 2 - 4.3 volts.

While the invention has been described in connection with specific embodiments thereof, it will be understood that the scope of the claims should not be limited by the preferred embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole.

CLAIMS

1. Lithium ion reversible insertion-type electrode material based on orthosilicate structure having the general formula:



wherein

M represents Mn^{2+} , Fe^{2+} or a mixture thereof;

D represents Mg^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cu^{2+} , Ti^{2+} , V^{2+} or Ca^{2+} ;

T represents Al^{3+} , Ti^{3+} , Cr^{3+} , Fe^{3+} , Mn^{3+} , Ga^{3+} , Zn^{3+} or V^{3+} ;

Q represents Ti^{4+} , Ge^{4+} , Sn^{4+} or V^{4+} ;

R represents V^{5+} , Nb^{5+} or Ta^{5+} ;

M, D, T, Q, R being elements residing in octahedral or tetrahedral sites;

s and p are the stoichiometric coefficient for S^{6+} (sulfate), P^{5+} (phosphate), respectively residing in the silicon tetrahedral sites;

the stoichiometric coefficients d, t, q, r, p and s being all positive and comprised between zero and 0.1;

$0 \leq x \leq 2$; $1 \leq m \leq 2$; and

$x + 2m + t + 2q + 3r = 4 - p - 2s$,

with the proviso that the lithium ion reversible insertion-type electrode material is not $\text{Li}_2\text{MnSiO}_4$ or $\text{Li}_2\text{FeSiO}_4$.

2. Lithium ion reversible insertion-type electrode material according to claim 1 characterized in that a crystal structure is related to one of those of lithium phosphate or that of lithium orthosilicate.

3. Lithium ion reversible insertion-type electrode material according to claim 1 or 2, further characterized as being orthosilicates containing SiO_4^{4-} tetrahedrons.

4. Lithium ion reversible insertion-type electrode material according to any one of claims 1 to 3 characterized in that more than one lithium ion is extracted or inserted per unit formula.

5. Lithium ion reversible insertion-type electrode material according to any one of claims 1 to 4, characterized in that the material is of formula $\text{Li}_x\text{Fe}_f\text{Mn}_m[\text{Si}_{(1-p)}\text{P}_p\text{O}_4]$ wherein $f + m \leq 1.2$; $p \leq 0.1$; $0 \leq x \leq 2$.
6. Lithium ion reversible insertion-type electrode material according to any one of claims 1 to 4, characterized as being: $\text{Li}_{1.4}\text{Fe}_{1.2}\text{Mn}_{0.1}\text{SiO}_4$, and $\text{Li}_{1.7}\text{Mn}_{0.7}\text{Fe}_{0.3}[\text{Si}_{0.7}\text{P}_{0.3}\text{O}_4]$.
7. Electrical generator having at least one positive electrode and one negative electrode characterized in that the at least one positive electrode contains the lithium ion material as defined in any one of claims 1 to 6 and the at least one negative electrode is a source of lithium ion.
8. Electrical generator according to claim 7 characterized in that the negative electrode is metallic lithium, a lithium alloy, a lithium intercalation compound carbon or carbonaceous matters resulting from the pyrolysis of organic derivatives, a lithium-titanium spinel $\text{Li}_{1+y}\text{Ti}_{2-x}/_4\text{O}_4$ wherein $0 \leq x$ and $0 \leq y \leq 1$ and its solid solutions with other spinels, or a lithium-transition metal mixed nitride and mixtures thereof.
9. Electrical generator according to claim 8 wherein the lithium alloy is a nanodispersion in lithium oxide.
10. Electrical generator according to claim 7 characterized in that a conductive additive is present in the positive electrode.
11. Electrical generator according to claim 10 characterized in that the conductive additive in the positive electrode material is carbon.
12. Electrical generator according to claim 7 characterized in that the positive electrode comprises a material of formula $\text{Li}_x\text{Fe}_f\text{Mn}_m[\text{Si}_{(1-p)}\text{P}_p\text{O}_4]$ wherein $f + m \leq 1.2$; $p \leq 0.1$ and $0 \leq x \leq 2$.

13. Electrical generator according to claim 7 characterized in that the at least one positive electrode further contains another lithium ion reversible insertion-type electrode material.

14. Electrical generator according to claim 13 characterized in that the another lithium ion reversible insertion-type electrode material is a lamellar dichalcogenide, a vanadium oxide VO_x , $2.1 \leq x \leq 2.5$ or a Nasicon-related material.

15. Electrical generator according to claim 14 wherein the Nasicon-related material is $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$.

16. Electrical generator according to any one of claims 7 to 11 characterized in that the at least one positive electrode contains a polymeric binder.

17. Electrical generator according to claim 16 characterized in that the polymeric binder is an homopolymer or copolymer of tetrafluoroethylene or an ethylene-propylene-diene terpolymer.

18. Electrical generator according to claim 17 characterized in that the at least one positive electrode contains:

- an aprotic solvent, and
- a salt;

said salt having a cation being at least in part Li^+ .

19. Electrical generator according to claim 16 characterized in that the polymeric binder possesses ionic conductivity.

20. Electrical generator according to claim 18 characterized in that the polymeric binder is a polyether in which at least one lithium salt is dissolved.

21. Electrical generator according to claim 20, wherein the polyether is crosslinked.

22. Electrical generator according to claim 16 characterized in that the polymeric binder is swollen by an aprotic solvent and contains a salt; said salt having a cation being at least in part Li^+ .
23. Electrical generator according to claim 16 characterized in that the polymeric binder is a polyether, a polyester, a methylmethacrylate-based polymer, an acrylonitrile-based polymer, or a vinylidene fluoride-based polymer.
24. Electrical generator according to claim 18 or 22 characterized in that the aprotic solvent is ethylene carbonate, propylene carbonate, dimethylcarbonate, diethylcarbonate, methyl-ethylcarbonate, γ -butyrolactone, a tetraalkylsulfamide, a dialkylether of a mono-, di-, tri-, tetra- or higher oligo- ethylene glycols of molecular weight lower or equal to 2000, or a mixture thereof.
25. Electrical generator of the supercapacitor type characterized in that at least one of the electrodes of the supercapacitor comprises the lithium ion reversible insertion-type electrode material as defined in any one of claims 1 to 4.
26. Variable optical transmission device constructed from transparent semi-conductor coated glass or plastic and two electrodes separated by a solid or gel electrolyte, characterized in that at least one of the electrodes contain the lithium ion reversible insertion-type electrode material as defined in claim 1.
27. Variable optical transmission device according to claim 26 characterized in that at least one of the electrodes is obtained by laying a film of the lithium ion reversible insertion-type material as defined in claim 1 on a transparent semi-conductor coated glass or plastic by a vacuum deposition technique, sputtering, or from a sol-gel precursor.