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(54) Titre : COMPOSES REDOX A SURFACE MODIFIEE ET ELECTRODE COMPOSITE OBTENUE AU MOYEN DE CEUX-CI

(54) Title: SURFACE MODIFIED REDOX COMPOUNDS AND COMPOSITE ELECTRODE OBTAIN FROM THEM

(57) **Abrégé/Abstract:**

The invention relates to surface modified carbon-coated redox LiFePO_4 , reversible to lithium ion, and to battery cathode coating obtained from. In view to improve properties of carbon-coated lithium iron phosphate, inventors, after intensive R&D activities, discovered that its usage value could be efficiently improved, by taking advantage of carbon functionalities (such as but not limited to $-\text{COOH}$, $-\text{OH}$, $-\text{COR}$) present on the carbon surface from the C-LiFePO_4 synthesis or post-treatment to induce carbon surface modification by grafting of various chemical functionalities on carbon surface (designed as "SMC- LiFePO_4 "), such as a better cathode powder wettability and a better adhesion between cathode particles and the binder.

Patent Application:**Resume**

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- 15 treatment to induce carbon surface modification by grafting of various chemical functionalities on carbon surface (designed as " SMC-LiFePO_4 "), such as a better cathode powder wettability and a better adhesion between cathode particles and the binder.

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1. Field of the invention:

The invention relates to surface modified carbon-coated redox compounds, reversible to lithium ion, and to battery cathode coating
5 obtained from them.

2. Description of the prior art:

Coating technology is one of main challenge in battery field,
10 particularly in term of economic. Manufacturing technologies should be adapted and optimized depending on used components, mainly in the case of Li-Ion and Lithium Metal Polymer (LMP) batteries. Cathode material is a key component among all, most difficult to process as highly load mineral powder coating formulation. Cathodes materials
15 such as LiMn_2O_4 , LiCoO_2 , $\text{Li}_{(1+x)}\text{V}_3\text{O}_8$ or LiNiO_2 are commonly used in commercials and/or prototypes lithium batteries. A huge effort is now dedicated to introduce lithium iron phosphate (LiFePO_4), such as disclosed in US 5,910,382, US 6,514,640, US 6,447,951, and US 6,153,333, as a substitute cathode material essentially based on
20 cost, performance and safety concerns. It is obvious to the expert that LiFePO_4 formula represent also other complex oxides (e.g. LiMXO_4) in which the oxygen is bound to a non metal (X) such as Phosphorus, Sulfur and Silicon elements which said complex oxides having the same intrinsic low electronic conductivity and made of at
25 least one transition metal such as Fe, Mn, Ni, Co in which additive can be made and stoichiometry can be more or less deficient or in excess on one constituent. LiFePO_4 present a low intrinsic electronic conductivity, this difficulty can be overcome by coating LiFePO_4 particle with a carbon layer (designed as "C- LiFePO_4 "), such as those
30 obtained by pyrolysis of an organic precursor (see for example US 6,855,273 B2). Since LiFePO_4 or C- LiFePO_4 is usually made as fine particle material, to improve power characteristics and compensate limited lithium-ion diffusivity in the bulk, it further develop the surface as determined by BET, usually in the range of $14 \text{ m}^2/\text{g}$ (more
35 generally in the $5\text{-}20 \text{ m}^2/\text{g}$) in the case of C- LiFePO_4 and as a

consequence requires usually more binder to achieve composite electrode cohesion and adhesion than coarser particle such as LiCoO_2 .

5 Generally speaking, two main processes could be used to prepare composite cathode coating. In the field of Li-Ion battery technology, a porous cathode coating on current collector is prepared by solvent-based formulation containing a dispersion of cathode material, carbon particles, as conductivity enhancer, and a binder. This porous cathode is subsequently filled by an electrolytic
10 solution. In Lithium Metal Polymer (LMP) technology, a mix of cathode material, carbon particles and ion conductive polymer, such as poly(ethylene oxide) derivatives, is coated on a current collector by solvent-based coating or directly by dry extrusion technology.

15 Development of battery coating using carbon-coated LiFePO_4 cathode introduce several specific constraints, carbon coating increase hydrophobic properties and modified surface tension, leading to altered interaction with other components and consequently induce change in physical properties such as wettability of porous cathode
20 coating, binder-particule adhesion or viscosity of extrusion formulation. Moreover, specific morphology of carbon-coated LiFePO_4 , due to high surface developed by carbon coating, is an important point to design efficient cathode coating formulation.

Generally, in addition, cathode composite comprising: C- LiFePO_4 ,
25 binder and conductive carbon dispersed in the binder/electrolyte, represent main weight of battery cathode coating, close to 60% in LMP technology and there is a need to decrease the dead weight components such as the binder making it effective with a minimal amount.

30 In view to improve properties of carbon-coated lithium iron phosphate, inventors, after intensive R&D activities, discovered that its usage value could be efficiently improved, by taking advantage of carbon functionalities (such as but not limited to $-\text{COOH}$, $-\text{OH}$, $-\text{COR}$) present on the carbon surface from the C- LiFePO_4 synthesis or post-
35 treatment to induce carbon surface modification by grafting of various chemical functionalities on carbon surface (designed as

"SMC-LiFePO₄"), such as a better cathode powder wettability and a better adhesion between cathode particles and the binder.

3. Description of the invention:

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Surface modification of carbon-coated LiFePO₄ was efficient to improve usage properties of C-LiFePO₄ through grafting of various chemical functionalities on carbon surface (designed as "SMC-LiFePO₄"), inventors qualified several of them during R&D activities as described below.

10

Waterborne-coating of battery electrode avoids or reduce use of organic solvents and are popular within lithium battery industries, first for anode coating and more recently cathode coating (see for example US 5,721,069, US 6,399,246, US 6,096,101, WO 04/045007, JP 2003-157852)¹. Hydrophobic properties of C-LiFePO₄ is a drawback to produce waterborne coating solution, grafting carbon surface with ionic species such as -COOH, -COOLi, -SO₃H and -SO₃Li or with polymers such as poly(ethylene oxide) have increase C-LiFePO₄ processability and as such preparation of battery grade electrode coating.

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Due to carbon coating, C-LiFePO₄ develop frequently higher surface area than alternative materials, typically in the range of 5-20 m²/g, comparatively LiCoO₂ cathode material present typically a < 1 m²/g surface area. This high surface area is a drawback for coating formulation with influence on parameters such as quantity of binder and porosity. Furthermore, C-LiFePO₄ is usually made of very fine particles or larger agglomerates made of fine particles and binder dispersion and adhesion with particles of C-LiFePO₄ must be as efficient as possible with a minute amount of binder. Grafting on carbon surface with reactive species such as but not limited to

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¹ Add reference of IMLB-12 publication Nara ECS Characterization of Sodium Carboxymethylcellulose Binder with HPLC - S.-S. Hwang and J.-H. Park (Samsung Advanced Institute of Technology, and Enhancement of Adhesion Property in SBR-Based Binder System for Li-Ion Battery - J.-H. Park (Samsung Advanced Institute of Technology), K.-W. Cho, D.-H. Lee, T.-B. Oh (POSTECH), B.-J. Jung, and S.-H. Lee (Samsung SDI Co., Ltd.).

-COOH, -OH, acrylate, allyl, styrene, or epoxyde as allowed efficient C-LiFePO₄/binder formulation design. It has been especially possible to prepare composite electrode where binder includes reactive species (such as but not limited to epoxyde, oxazoline, aziridine, isocyanate, amine) able to react with SMC-LiFePO₄ containing -COOH surface groups to form ester or amide linkage. Synthesis of SMC-LiFePO₄ containing polymerizable (and/or condensable) species allow preparation of composite obtain by co-polymerisation (and/or condensation) of SMC-LiFePO₄ with binder bearing polymerizable (and/or condensable) functionalities such as co-polymerization of allyl grafted SMC-LiFePO₄ with a binder formulation including acrylate polymers. By extension, inventors have also been able to prepare binder grafted SMC-LiFePO₄ through grafting of polymer segments bearing at least one polymerizable functionality such as styrene end-capped poly(ethylene oxide), inducing particle/particle adhesion.

Grafting of ionic species such as -COOLi or -SO₃Li also proved valuable to increase wettability of composite electrode resulting in improve cathode filling especially by liquid electrolyte and induce surface ionic conductivity beneficial to electrochemical properties. Surface tension modification could also be obtained by grafting with hydrophilic polymers such as poly(ethylene oxide derivatives).

Use of SMC-LiFePO₄ is also of interest for extrusion technology either for lithium metal polymer or Li-Ion batteries² through improvement of rheological properties induced by modification of surface tension by ionic species such as -COOLi or -SO₃Li or grafting of polymers with improved compatibility with polymer electrolyte in LMP and/or tensio-active properties.

Modification of C-LiFePO₄ surface to graft functionality could be done by a large scope of industrial technology in some case during preparation of C-LiFePO₄ or by a subsequent chemical treatment,

² Such as operate by Gaia

opening the way to design SMC-LiFePO₄ able to match battery manufacturers needs through molecular engineering.

For example, -COOH grafted SMC-LiFePO₄ could be prepared by reaction
5 by oxydation with CO₂ gas at 500-800°C, by cold plasma treatment
under O₂ or CO₂, by diazotation with -COOH containing chemical
species, by diels-alder addition of species such as fumaric acid, by
addition of disulfide bearing -COOH, by addition of benzotriazole
bearing -COOH, by addition of azo compounds bearing -COOH. Those
10 SMC-LiFePO₄ could be further use to graft another species for example
through condensation with -OH or -NH₂, or reaction with isocyanate,
epoxyde, aziridine, or oxazoline species to produce ester or amide
linkage, allowing grafting of a broad set of functionality such as
polymers or polymerizable groups. -COOH groups could also be used to
15 initiate polymerization of monomers.

We have described possibilities with -COOH groups to illustrate that
possibilities to design SMC-LiFePO₄ are extremely large and not
limited to specific examples. It will be easy to imagine a lot of
20 possibilities to prepare SMC-LiFePO₄ without departing from present
invention.

An other aspect of the invention is to make use of C-LiFePO₄
containing carbon nanotubes at its surface as illustrated in figure
25 1. Such nanotube could be surface treated as described in the present
invention to provide SMC-LiFePO₄ and cathode containing to improve
mechanical and chemical adhesion with the binder. Such modified
SMC-LiFePO₄ is also improving electronic conduction pathway.
Surprisingly, inventors discovered that C-LiFePO₄ bearing nanotubes
30 already improved electrochemical properties without any additional
surface treatment, probably through improved electronic pathway.

An abundant literature described process to modify carbon surface,
see for example US 22053768, US 2413834, US 21036994, US 06503311,
35 US 23101901, US 22096089, US 2401814, US 23180210, EP 01078960,
"Chemically modified carbon fibers and their applications" by I. N.

Ermolenko, I. P. Lyubliner, and N. V. Gulko, VCH, New York and Germany, 1990, 304 pp, "Plasma surface treatment in composites manufacturing", T. C. Chang, Journal of Industrial Technology, Volume 15, Number 1, November 1998 to January 1999.

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An abundant literature described possible modification of carbon surface through grafting by polymers such as disclosed in "Functionalization of carbon black by surface grafting of polymers", N. Tsubokawa, Prog. Polym. Sci., 17, 417 (1992), and
10 "Functionalization of Carbon Material by Surface Grafting of Polymers ", N. Tsubokawa Bulletin of the Chemical Society of Japan Vol. 75, No. 10 (October, 2002).

Having generally described this invention a further understanding can
15 be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

Example 1: Carbon-coated LiFePO_4 (product of Phostech Lithium Inc, Canada; 200 g), designed as "C- LiFePO_4 ", was treated 24 hours under
20 reflux in a 600 ml toluene solution of maleic anhydride (product of Aldrich; 20 g). After filtration, surface modified carbon-coated LiFePO_4 (designed as "SMC- LiFePO_4 ") was washed several times with toluene, and subsequently dried under vacuum at 80°C during 24 hours. SMC- LiFePO_4
25 contains grafted $-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$ anhydride groups. Part of this material was treated by LiOH or KOH aqueous solution to produce $-\text{COOLi}$ or $-\text{COOK}$ grafted SMC- LiFePO_4 , from which a part has been treated by HCl aqueous solution to produce $-\text{COOH}$ grafted SMC- LiFePO_4 .

30 **Example 2:** Water solution of disulfide $\text{LiSO}_3-\delta-\text{S}-\text{S}-\delta-\text{SO}_3\text{Li}$ (5 g) was thoroughly mixed with C- LiFePO_4 (product of Phostech Lithium Inc; 100 g). After removal of water, product was heated at 180°C during 4 hours under argon, washed overnight in a soxhlet extractor and

then dry under vacuum at 80°C during 24 hours. SMC-LiFePO₄ contains grafted lithium sulfonate groups.³

Example 3: A batch of LiFePO₄ was synthesized by melting at 1000°C under argon (1 hour), in a graphite crucible, Fe₂O₃ (product of Aldrich; 1 mole), (NH₄)₂HPO₄ (product of Aldrich; 2 moles) and Li₂CO₃ (product of Limtech, Canada; 1 mole). LiFePO₄ (94% purity by DRX) was then ground to a 2 μm mean particle size powder, with a planetary ball mill. LiFePO₄ powder was then mixed in an alumina mortar with 4 %wt. acetylene black (product of Chevron Phillips Chemical Company) and subsequently treated by a mechanofusion process at 1000 rpm during 1 hour to produce acetylene black-coated LiFePO₄. C-LiFePO₄ was then treated 2 hours at 700°C with a water steam under a CO/CO₂ gas flow. SMC-LiFePO₄ contains grafted -OH and -COOH groups.

15

Example 4: LiFePO₄ powder, as disclosed in example 3, was mixed in an alumina mortar with 3 %wt. FW 200 carbon black (product of Degussa, Germany) and subsequently treated by a mechanofusion process at 1000 rpm during 1 hour to produce C-LiFePO₄. SMC-LiFePO₄ contains grafted -COOH groups.

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Example 5: LiFePO₄ powder, as disclosed in example 3, was mixed with a dispersion of FW 200 carbon black in a polyvinyl alcohol (PVA, product of Aldrich) water solution such as FW 200 and PVA accounts respectively for 2% wt. and 1% wt. of LiFePO₄. After water removal, mixture was treated at 600°C for 1 hour under an argon flow. SMC-LiFePO₄ contains grafted -COOH groups.

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Example 6: Carbon-coated LiFePO₄ (product of Aldrich, 50 g) was microwave plasma-treated (2.45 Ghz, 300 W) during 30 sec in pure O₂ atmosphere (1 mbar). SMC-LiFePO₄ contains grafted -COOH and -OH.⁴

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Example 7: LiFePO_4 powder was mixed in an alumina mortar with 4 %wt. carbon black FW 1 (product of Degussa, Germany) and subsequently treated by a mechanofusion process at 1000 rpm during 1 hour to produce carbon black-coated LiFePO_4 . C- LiFePO_4 (50 g) was refluxed in a degassed water solution (300 ml) of δ -(1-benzotriazolyl)-butanesulfonic acid (2 g) during 8 hours. After filtration of reaction media, treated C- LiFePO_4 was washed several times with water. SMC- LiFePO_4 contains grafted sulfonic acid groups. Experiment was repeated with respectively benzotriazole-5-carboxylic acid (product of Aldrich) and 5-amino-benzotriazole (product of Lancaster Synthesis Ltd)⁵ to produce SMC- LiFePO_4 containing respectively grafted carboxylic acid and amino groups.

Example 8: C- LiFePO_4 (\approx 200 g) was synthesized as disclosed in example 3 and 4 of US 2004/0151649 by a precipitation/thermal treatment of LiFePO_4 followed by lactose impregnation/pyrolysis. C- LiFePO_4 was then mixed in water (200 ml) with Orange G azo compound with sodium sulfonate previously exchanged for lithium sulfonate groups (product of Aldrich; 5 g) for 30 minutes and, after solvent evaporation, irradiated three times 1 minute in a 700 W microwave oven. SMC- LiFePO_4 was then washed overnight in a soxhlet extractor and then dry under vacuum at 80°C during 24 hours. SMC- LiFePO_4 contains grafted lithium sulfonate groups. A similar experiment has been performed with azobenzene 4-carboxylic acid providing SMC- LiFePO_4 containing grafted -COOH groups.

Example 9: SMC- LiFePO_4 (10 g) containing grafted carboxylic acid groups was dispersed in an ethyl acetate (50 ml) solution of A 20-20 polyalkylene glycol monoallyl ethers (product of Clariant; 4 g). The mixture was cooled to 0°C and 1,3-dicyclohexyl carbodiimide (product of Aldrich, DCC; 200 mg) in ethyl acetate (5 ml) was added slowly over the course of 30 minutes, followed by pyridine catalyst. The reaction mixture was stirred at room temperature overnight. After filtration, powder was washed several times with ethyl acetate and water. SMC- LiFePO_4 contains allyl polymerizable groups. Similar experiments were repeated by replacing A 20-20 respectively with

2 mmoles of allyl alcohol, 1,6-hexanediol vinyl ether, 2-hydroxyethyl methacrylate, N-(hydroxymethyl)acrylamide, N-(4-hydroxyphenyl)maleimide, Noigen[®] RN-40 polyoxyethylene alkylphenyl ether (product of Dai-Ichi Kogyo Seiyaku Co., Japan) with DCC (2 mmoles)⁶ and pyridine catalyst to prepared SMC-LiFePO₄ containing respectively allyl, vinyl ether, methacrylate, acrylamide, maleimide and CH₃-CH=CH- δ - polymerizable groups.

Example 10: SMC-LiFePO₄ (2 g) containing grafted -SO₃Li groups was reacted in water with 1-ethyl-3-methylimidazolium (EMI) chloride (product of Aldrich, 100 mg). After filtration, product was washed several times with water and dried under vacuum at 80°C. SMC-LiFePO₄ contains grafted EMI sulfonate groups. Similar experiments were repeated by replacing EMI chloride with 1-butyl-1-methylpyrrolidinium (BMP) chloride (product of Merck, Germany) to produce SMC-LiFePO₄ containing grafted BMP sulfonate groups.

Example 11: SMC-LiFePO₄ (2 g) containing grafted -SO₃Li groups was reacted in water with diallyldimethylammonium (DADMA) chloride (product of Ciba Chemical Specialities, Switzerland; 100 mg). After filtration, product was washed several times with water and dried under vacuum at 80°C. SMC-LiFePO₄ contains grafted polymerizable allyl groups. Similar experiments were repeated by replacing DADMA chloride with (2-methylpropenoyloxyethyl)trimethylammonium (META) chloride (product of Ciba Chemical Specialities; 100 mg) to produce SMC-LiFePO₄ containing grafted polymerizable methacrylate groups.

Example 12: SMC-LiFePO₄ (50 g) containing grafted carboxylic acid groups was dispersed in an ethyl acetate (200 ml) solution of monoaminated ethylene oxide/propylene oxide copolymer Jeffamine M-2070 (product of Huntsman, USA; 20 g). 1,3-dicyclohexyl carbodiimide (400 mg) in ethyl acetate (5 ml) was added slowly over the course of 30 minutes. The reaction mixture was stirred at room temperature 24 hours. After filtration, powder was washed several times with ethyl acetate and

water. SMC-LiFePO₄ contains grafted Jeffamine M-2070 through amide linkage. A similar experiment has been performed by replacing Jeffamine[®] M-2070 with Surfonamine[®] L-300 (product of Hunstman; 20 g) to produce SMC-LiFePO₄ containing grafted Surfonamine[®] L-300 through amide linkage.

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Example 13: In a glove box, SMC-LiFePO₄ (3 g), containing grafted A 20-20 polyalkylene glycol monoallyl ethers (as disclosed in example 8), was mixed in acetonitrile (15 ml) with EBN-1010 graphite particles (product of Superior Graphite, USA; 250 mg), a terpolymer based on ethylene oxide, methyl-glycidyl ether and allylglycidyl ether (80:15:5 molar ratio; 1.7 g) and polyethylene glycol (600) diacrylate (product of Sartomer, France; 500 mg). The mixture is stirred at room temperature for about 12 hours, then 2,2'-azobis[2-(2-imidazolin-2-yl)propane] bis(trifluoromethanesulfonyl)imide (TFSI) salt (product of Wako, Japan, previously exchanged with LiTFSI in water; 17.5 mg) are added and the solution is again stirred for 90 minutes. After being coated as a film 30 μ m thick, the material is heated under an inert atmosphere at 80°C for 24 hours. Thus was obtained a battery grade cross-linked cathode coating, containing SMC-LiFePO₄, in the form of an interpenetrated network (IPN) between polymers and SMC-LiFePO₄

Example 14: SMC-LiFePO₄ (8 g), containing grafted -COOH groups was thoroughly mixed with EBN-1010 graphite particles (1 g) and water-based polyoxazoline EPOCROS WS-700 solution (product of Nippon Shokubai, Japan; 4 g)⁷. After being coated as a film 60 μ m thick, the material is heated at 120°C for 1 hour. Thus was obtained a battery grade Li-Ion cathode coating, containing SMC-LiFePO₄, with chemicals bonds between binder and SMC-LiFePO₄, obtained by oxazoline and -COOH reaction.

Example 15: SMC-LiFePO₄ (2.82 g), containing grafted -COOH and -OH groups, was mixed in water (1.8 ml) with EBN-1010 graphite particles (product of Superior Graphite; 12 mg) and LHB-108P waterborne modified

styrene-butadiene copolymer suspension (product of LICO Technology Corp., Taiwan, available through Pred Materials International Inc., USA; 40 mg). After being coated as a film 50 μ m thick, the material is heated at 60°C during 2 hours and further under an inert atmosphere at 80°C for 24 hours. Thus was obtained a battery grade waterborne cathode coating, containing SMC-LiFePO₄.

Example 16: Add experiment with latex functionalized with epoxyde groups at the surface combined with -COOK grafted SMC-LiFePO₄.

Example 17: Add experiment with latex functionalized with oxazoline groups (Nippon Shokubai) at the surface combined with -COO,NH₄ grafted SMC-LiFePO₄.

Example 18: Add experiment with Dow Corning epoxy-silane Z-6040 to prepared SMC-LiFePO₄ with silane functionalities and subsequent preparation of a silicate/LiFePO₄ cathode coating.

Example 19: Add experiment with a SMC-LiFePO₄ containing onium salt (such as imidazolium) to prepare a ionic liquid battery.

Example 20: Add experiment with a SMC-LiFePO₄ containing a polymerizable groups able to copolymerize with a gelification agent in a ionic liquid composition.

Example 20: Extrusion composition with a polymer.

Example 21: Effect of POE grafting on surface tension.

Example 22: Coating with Zeon type rubber-like latex + SMC-LiFePO₄ grafted with -COOLi with better wettability (reduce time to fill with a liquid electrolyte).

Example 23: Add experiment with "Muller-ELF" polymer electrolyte based on diol-aluminum salt implying a role of -COOH on SMC-LiFePO₄-electrolyte interaction through -COO•Al•O-R interaction.

Although the present invention has been described hereinabove by way of preferred embodiments thereof, it can be modified, without departing from the spirit and nature of the subject invention as defined in the
5 appended claims.

Claims:

Claim 1

Process to make surface modified C-LiFePO₄ cathode material for use
 5 in a battery composite electrode of the general formula:
 Y-C-LiFePO₄ which comprises the steps of:
 Synthesizing particles or agglomerates of particle of C-LiFePO₄ on
 which the C is attached to the LiFePO₄ particles.
 Grafting functional organic moieties Y on some of the carbon sites in
 10 order to improve cathode material processability and electrochemical
 properties.
 Said cathode material being made of elementary particles whose
 dimension are comprised in the range on 1 nanometer to 5 microns for
 at least 90% of the particles present or not as agglomerates of such
 15 elementary particles whose dimensions are comprised between 10
 nanometers and 10 microns for at least 90 % of the particles.

Claim 2

Process as in claim 1 in which functionalities could be at least one
 20 or combination of:
 •-COOCO-, COOR, OR, aldehyde, cetone, quinone, SO₃R, SO₂R, PO₂R,
 NH₂, Br, Cl, I
 •polymers and copolymers
 •surfactant
 25 •reticulable, condensable functionalities
 R is an organic group or H, alkali metal.

Claim 3

Process according to Claim 1 in which the synthesis of C-LiFePO₄ is
 30 made in condition of temperature and gaz atmosphere such as to
 generate functionalities on the C.

Claim 4

Process according to claim 3 in which oxygenated carbon product are
 35 grafted through control oxidation: cetone, aldehyde, quinone, COOR
 and OR.

Claim 5

Process according to claims 1 to 4 in which the C-coating is made by pyrolysing a C precursor in one or more separate steps after the
5 LiFePO₄ synthesis using C precursor, chemical atmosphere and temperature in order to coat C attached to the LiFePO₄ particle or agglomerate of particles and to induce organic functionalities on the C in one or more steps.

10 Claim 6

Process according to claims 1 to 5 in which the C coating is anchored mechanically on the LiFePO₄ particles or particle agglomerates, said C being surface functionalized before or after attaching the C to LiFePO₄.

15

Claim 7

Process according to claim 1 to 6 comprising one additional step through which the crosslinkage or condensable organic moiety is chemically linked with the cathode composite binder to improve
20 adhesion between the binder and the LiFePO₄ particle or agglomerate of particles.

Claim 8

Process according to claim 7 in which the binder is contacting most
25 of the surface of the LiFePO₄ particles or agglomerate of Particle or alternatively present in the form of a micro dispersion to minimize the amount of binder needed to achieve composite coherence and adhesion.

30 Claim 9

Process according to claim 8 in which functionalities induce tensio-active properties improving wettability of the composite by the electrolyte and/or adhesion of the particle to the binder.

35 Claim 10

Cathode material and cathode composite formulation obtained from any of the process describes in the claim 1 to 9.

Claim 11

5 Carbon coated LiFePO_4 cathode materials bearing organic functionalities on its surface.

Claim 12

10 Material as in claim 9 where functionalities are ionic species choosen from: $-\text{COOH}$, $-\text{OH}$, $-\text{SO}_3\text{H}$, $-\text{NH}_2$, $-\text{PO}_2\text{H}$ and their salts.

Claim 13

15 Material as in claim 10 where ionic species are modified to form amide and/or ester linkage

Claim 14

Carbon coated LiFePO_4 cathode materials bearing polymerizable and/or condensable functionalities on its surface.

20 Claim 15

Composite electrode in which binder is link to carbon surface through linkage with functionalities.

Claim 16

25 Composite electrode in which particles are link through grafted functionalities including through polymerization, condensation, crosslinking reaction.

Claim 17

30 Carbon coated LiFePO_4 cathode materials as in claim 9-16 where carbon layer contains nanotubes on its surface.

Claim 18

35 Carbon as in claim 17 where nanotube are surface modified according to claim 1 to 17

Claim 19

Composite electrode containing a material as in claim 17 to 19 in which C-LiFePO₄ particles and/or agglomerate are chemically or mechanically adherent to the binder.

Application number: numéro de demande: 2, 506, 104

Figures: 1

Pages: 1

DRW-1P

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