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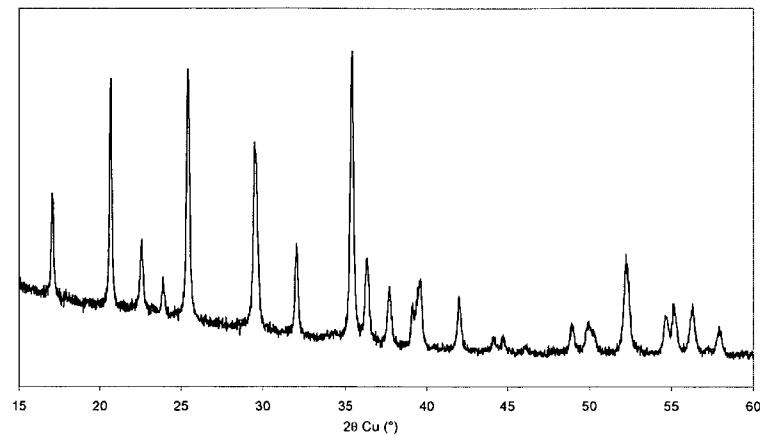
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(54) Title: SYNTHESIS OF CRYSTALLINE NANOMETRIC LiFeMPO₄

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(57) Abstract: The present invention relates to lithium secondary batteries and more specifically to positive electrode materials operating at potentials greater than 2.8 V vs. Li⁺/Li in non-aqueous electrochemical cells. In particular, the invention relates to crystalline nanometric olivine-type LiFe_{1-x}M_xPO₄ powder with M is Co and/or Mn, and 0<x<1, with small particle size and narrow particle size distribution. A direct precipitation process is described, comprising the steps of: - providing a water-based mixture having at a pH between 6 and 10, containing a dipolar aprotic additive, and Li^(II), Fe^(III), P^(V), and Co^(III) and/or Mn^(III) as precursor components; - heating said water-based mixture to a temperature less than or equal to its boiling point at atmospheric pressure, thereby precipitating crystalline LiFe_{1-x}M_xPO₄ powder. An extremely fine particle size is obtained of about 80 nm for Mn and 275 nm for Co, both with a narrow distribution. The fine particle size is believed to account for excellent high-drain properties, while minimizing the need for conductive additives. The narrow distribution facilitates the electrode manufacturing process and ensures a homogeneous current distribution within the battery.



PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, **Published:**
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG). — *with international search report*

Synthesis of crystalline nanometric LiFeMPO₄

The invention relates to a crystalline nanometric LiFe_{1-x}M_xPO₄ (LFMP) powder with small particle size and narrow particle size distribution for use as positive electrode material in Li batteries. It also describes a preferred manufacturing method by precipitation at low temperature and atmospheric pressure of the crystalline nanometric powder.

Since the original work of Padhi et al. (JES, 144 (1997), 1188), phospho-olivines LiMPO₄ (with M = Fe, Ni, Co, Mn, ...) have appeared to be potential candidates to be used as cathode materials for Li batteries. Among all these isostructural compositions, LiFePO₄ was the most investigated and its commercialization is now a reality thanks to very high performances in term of reversible capacity, rate properties and cycle life (International Publication Number WO2004/001881 A2).

LiCoPO₄ (Amine et al., ESSL, 3, (2000), 178) and LiMnPO₄ (Okada et al., J. Power Sources, 97-98 (2001) 430), due to their higher redox potential values oft 4.8 V and 4.1 V vs. Li respect., are of particular interest because of the higher energy density they offer compared to LiFePO₄ (3.5V vs. Li, Chen et al., JES, 149 (2002) A1184).

However, it is now well known that these phospho-olivines materials suffer from poor electronic and ionic conductivity (Delacourt et al., JES, 152 (2005) A913) so that the need for optimising the microstructure of these compounds is essential. Striebel et al. (JES, 152, (2005), A664) insisted on the fact that, even if the matrix conductivity has been improved by conductive coating, the battery developer would welcome so-far nonexistent compounds having a primary particle size in the 50 to 100 nm range and, overall, attempts should be made to minimise the particle size distribution, in order to yield better power efficiency.

Most promising results on mixed metal phosphates such as LiFe_{1-x}Mn_xPO₄ materials were obtained on C/LiFe_{0.4}Mn_{0.6}PO₄ composites, in which C acts as a sintering inhibitor. This

approach leads to mixed C/LiFeMnPO₄ composites with particles in the 100 to 200 nm range (Mi et al., Mater. Sci. Eng., 129 (2006) 8). Similar results were obtained by Lloris et al. (ESSL, 5 (2002) A234), on pure LiCoPO₄ with small particles in the 200 to 300nm range. No data were published on LiFe_{1-x}Co_xPO₄ materials so far.

5

In addition to the small particle size, emphasis must be put on narrowing the particle size distribution in order to ensure a homogeneous current distribution in the electrode and thus achieve better battery performances, in particular high power efficiency and long cycle life. The present invention therefore aims at providing a crystalline LFMP powder 10 with small particle size and narrow particle size distribution.

To this end, a process is disclosed yielding metal phosphate powders offering essential improvements over the materials cited above.

15 The invented process for the synthesis of crystalline LiFe_{1-x}M_xPO₄ powder where M is one or both of Co and Mn, and 0<x<1, preferably 0.4<x<0.95, comprises the steps of:
- providing a water-based mixture having a pH between 6 and 10, containing a dipolar aprotic additive, and Li^(I), Fe^(II), P^(V), and one or both of Co^(II) and Mn^(II) as precursor components;

20 - heating said water-based mixture to a temperature less than or equal to its boiling point at atmospheric pressure, thereby precipitating crystalline LiFe_{1-x}M_xPO₄ powder. The obtained powder can be subjected to a post-treatment by heating it in non-oxidising conditions.

25 A pH of between 6 and 8 is however preferred to avoid any precipitation of Li₃PO₄. The additive is preferably a dipolar aprotic compound without chelating or complexation propensity. The heating temperature of the water-based mixture of at least 60 °C is preferred.

30 The production of the crystalline LiFe_{1-x}M_xPO₄ powder or the thermal post-treatment can advantageously be performed in the presence of at least one further component, in

particular a carbon containing or electron conducting substance, or the precursor of an electron conducting substance.

It is useful to introduce at least part of the Li^(I) as LiOH. Similarly, at least part of the 5 P^(V) can be introduced as H₃PO₄. The pH of the water-based mixture can be obtained by adjusting the ratio of LiOH to H₃PO₄.

It is advisable to use a water-based mixture with an atmospheric boiling point of between 100 and 150 °C, and preferably between 100 and 120 °C. Dimethylsulfoxide (DMSO) is 10 preferably used as the dipolar aprotic additive. The water-based mixture advantageously contains between 5 and 50 %mol, and preferably between 10 and 30 %mol, of DMSO. A lower DMSO concentrations result in a coarser particle size distribution; higher concentrations limit the availability of water, forcing to increase the volume of the apparatus.

15

The step of post treatment of the LiFe_{1-x}M_xPO₄ is advantageously performed at a temperature of up to 675 °C, and preferably of at least 300 °C. The lower limit is chosen in order to enhance the crystallinity of the precipitated LiFe_{1-x}M_xPO₄; the upper limit is chosen so as to avoid the decomposition of the LiFe_{1-x}M_xPO₄ into manganese phosphides.

20

The electron conducting substance can be carbon, in particular conductive carbon or carbon fibres. Alternatively, a precursor of an electron conducting substance can be used, in particular a polymer or sugar-type macromolecule.

25 The invention also pertains to a crystalline LiFe_{1-x}Mn_xPO₄ powder with 0<x<1, preferably 0.4<x<0.95, for use as electrode material in a battery, having a particle size distribution with an average particle size d₅₀ of less than 100 nm, and preferably of more than 30 nm. The maximum particle size is preferably less than or equal to 500 nm. The particle size distribution is preferably mono-modal and the ratio (d₉₀ - d₁₀) / d₅₀ is advantageously 30 less than 1.5, preferably less than 1.3.

Another embodiment of this invention concerns a composite powder containing the above-defined crystalline LiMnPO_4 powder, and up to 10 %wt of conductive additive. A further embodiment concerns the electrode mix that can be prepared using this composite powder. Conductive carbons, carbon fibres, amorphous carbons resulting from

5 decomposition of organic carbon containing substances, electron conducting polymers, metallic powders, and metallic fibres are particularly well suited as conductive additives.

Another embodiment of this invention concerns the use of the composite powder for the manufacture of a lithium insertion-type electrode, by mixing said powder with a

10 conductive carbon-bearing additive.

The invention also pertains to a crystalline $\text{LiFe}_{1-x}\text{Co}_x\text{PO}_4$ powder with $0 < x < 1$, preferably $0.4 < x < 0.95$, for use as electrode material in a battery, having a particle size distribution with an average particle size d_{50} of less than 300 nm, and preferably of more than 30 nm.

15 The maximum particle size is preferably less than or equal to 900 nm. The particle size distribution is preferably mono-modal and the ratio $(d_{90} - d_{10}) / d_{50}$ is advantageously less than 1.5, preferably less than 1.1.

Another embodiment of this invention concerns a composite powder containing the

20 above-defined crystalline $\text{LiFe}_{1-x}\text{Co}_x\text{PO}_4$ powder, and up to 10 %wt of conductive additive. A further embodiment concerns the electrode mix that can be prepared using this composite powder. Conductive carbons, carbon fibres, amorphous carbons resulting from decomposition of organic carbon containing substances, electron conducting polymers, metallic powders, and metallic fibres are particularly well suited as conductive additives.

25

Another embodiment of this invention concerns the use of the composite powder for the manufacture of a lithium insertion-type electrode, by mixing said powder with a conductive carbon-bearing additive.

30 Compared to prior art, this product lists all the advantages needed for being considered as potential cathode material in lithium battery:

- the direct precipitation of crystalline LFMP at low temperature prevents any grain growth linked to sintering processes. Nanometric particle sizes are obtained. This reduces kinetic limitations due to Li ions transport within the particle, thereby enhancing the fast charge/discharge behaviour of the batteries.

5 - the narrow particle size distribution ensures a homogeneous current distribution within the battery. This is especially important at high charge/discharge rates, where finer particles would get more depleted than coarser ones, a phenomenon leading to the eventual deterioration of the particles and to the fading of the battery capacity upon use. Furthermore, it facilitates manufacturing of the electrode.

10

The atmospheric boiling point of the water-based mixture is advisably between 100 and 150 °C, preferably between 100 and 120 °C. Use is made of a water-miscible additive as a co-solvent that will increase the precipitate nucleation kinetics thus reducing the size of

15 the LiMnPO₄ nanometric particles. In addition to be miscible with water, useful co-solvents should be aprotic, i.e. show only a minor or complete absence of dissociation accompanied by release of hydrogen ions. Co-solvents showing complexation or chelating properties such as ethylene glycol do not appear suitable as they will reduce the kinetics of precipitation of LiMnPO₄ and thus lead to larger particle sizes. Suitable dipolar aprotic
20 solvents are dioxane, tetrahydrofuran, N-(C₁-C₁₈-alkyl)pyrrolidone, ethylene glycol dimethyl ether, C₁-C₄-alkylesters of aliphatic C₁-C₆-carboxylic acids, C₁-C₆-dialkyl ethers, N,N-di-(C₁-C₄-alkyl)amides of aliphatic C₁-C₄-carboxylic acids, sulfolane, 1,3-di-(C₁-C₈-alkyl)-2-imidazolidinone, N-(C₁-C₈-alkyl)caprolactam, N,N,N', N'-tetra-(C₁-C₈-alkyl)urea, 1,3-di-(C₁-C₈-alkyl)-3,4,5,6-tetrahydro-2(1H)-pyrimidone, N,N,N',N'-tetra-(C₁-C₈-alkyl)sulfamide, 4-formylmorpholine, 1-formylpiperidine or 1-formylpyrrolidine, N-(C₁-C₁₈-alkyl)pyrrolidone, N-methylpyrrolidone (NMP), N-octylpyrrolidone, N-dodecylpyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide or hexamethylphosphoramide. Other alternatives such as tetraalkyl ureas are also possible.
25 Mixtures of the abovementioned dipolar aprotic solvents may also be used. In a preferred embodiment, dimethylsulfoxide (DMSO) is used as solvent.

The Figures illustrating the invention are summarized as follows.

Fig. 1: XRD of the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ precipitate after 18 h reaction time.

Fig. 2: SEM picture of the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$.

5 Fig.3: Volumetric particle size distribution and cumulative distribution (% vs. nm) of the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$.

Fig. 4: XRD of the $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ precipitate after 18 h reaction time.

Fig. 5: SEM picture of the $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$.

Fig. 6: Volumetric particle size distribution and cumulative distribution (% vs. nm) of the

10 $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$.

The invention is further illustrated in the following examples.

Example 1: Synthesis of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$

15 In a first step, DMSO is added to an equimolar solution of 0.05 M $\text{Mn}^{(\text{II})}$ in $\text{MnNO}_3 \cdot 4\text{H}_2\text{O}$, 0.05 M $\text{Fe}^{(\text{II})}$ in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.1 M $\text{P}^{(\text{V})}$ in H_3PO_4 , dissolved in H_2O while stirring. The amount of DMSO is adjusted in order to reach a global composition of 50 %vol water and 50 %vol DMSO corresponding to respectively about 80 %mol and 20 %mol.

20 In a second step, an aqueous solution of 0.3 M $\text{LiOH} \cdot \text{H}_2\text{O}$ is added to the solution at 25 °C; the pH hereby increases to a value between 6.5 and 7.5. The final Li:Fe:Mn:P ratio is close to 3:0.5:0.5:1.

25 In a third step, the temperature of the solution is increased up to the solvent boiling point, which is 108 to 110 °C. After 18 h, the obtained precipitate is filtered and washed thoroughly with water. The pure crystalline $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ obtained is shown in Fig. 1.

30 The refined cell parameters are $a = 10.390 \text{ \AA}$, $b = 6.043 \text{ \AA}$; $c = 4.721 \text{ \AA}$, with a cell volume of 296.4 \AA^3 . This is in good agreement with Vegard's law specifying that, in case of solid solution, the cell volume of mixed product should be in-between that of end products (291 \AA^3 for pure LiFePO_4 , 302 \AA^3 for pure LiMnPO_4).

The picture on Fig. 2 shows monodisperse small crystalline particles in the 50-100nm range. The volumetric particle size distribution of the product was measured using image analysis. As shown in Fig. 3, the d50 values is about 80 nm, while the relative span,

5 defined as $(d90 - d10) / d50$, is about 1.2 ($d10 = 45$ nm, $d90 = 145$ nm).

Example 2: Synthesis of $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$

In a first step, DMSO is added to an equimolar solution of 0.05 M $\text{Mn}^{(\text{II})}$ in $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 0.05 M $\text{Co}^{(\text{II})}$ in $\text{CoNO}_3 \cdot 6\text{H}_2\text{O}$ and 0.1 M P(V) in H_3PO_4 , dissolved in H_2O while stirring.

10 The amount of DMSO is adjusted in order to reach a global composition of 50 %vol. water and 50 %vol. DMSO.

In a second step, an aqueous solution of 0.3 M $\text{LiOH} \cdot \text{H}_2\text{O}$ is added to the solution at 25 °C; the pH hereby increases to a value between 6.5 and 7.5. The, the final Li:Fe:Co:P ratio 15 is close to 3:0.5:0.5:1.

In a third step, the temperature of the solution is increased up to the solvent boiling point, which is 108 to 110°C. After 18 h, the obtained precipitate is filtered and washed thoroughly with water. The pure crystalline $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ obtained is shown in Fig. 4.

20 The refined cell parameters are $a = 10.292$ Å, $b = 5.947$ Å; $c = 4.712$ Å with a cell volume of 288.4 Å³. This is again in good agreement with Vegard's law specifying that, in case of solid solution, the cell volume of mixed product should be in-between that of end products (291 Å³ for pure LiFePO_4 , 284 Å³ for pure LiCoPO_4).

25 The picture on Fig. 5 shows monodisperse small crystalline particles in the 200-300nm range. The volumetric particle size distribution of the product was measured by using image analysis. As shown in Fig. 6, the d50 values is about 275 nm, while the relative span, defined as $(d90 - d10) / d50$, is about 1.0 ($d10 = 170$ nm, $d90 = 450$ nm).

Claims

1. A process for preparing crystalline $\text{LiFe}_{1-x}\text{M}_x\text{PO}_4$ powder where M is one or both of Co and Mn, and $0 < x < 1$, comprising the steps of:
 - 5 - providing a water-based mixture having a pH between 6 and 10, containing a dipolar aprotic additive, and $\text{Li}^{(\text{I})}$, $\text{Fe}^{(\text{II})}$, $\text{P}^{(\text{V})}$, and one or both of $\text{Co}^{(\text{II})}$ and $\text{Mn}^{(\text{II})}$ as precursor components;
 - heating said water-based mixture to a temperature less than or equal to its boiling point at atmospheric pressure, thereby precipitating crystalline $\text{LiFe}_{1-x}\text{M}_x\text{PO}_4$ powder.
- 10 2. Process according to claim 1, followed by a step of post-treatment of the $\text{LiFe}_{1-x}\text{M}_x\text{PO}_4$ powder by heating it in non-oxidising conditions.
- 15 3. Process according to claims 1 and 2, characterized in that the production of the crystalline $\text{LiFe}_{1-x}\text{M}_x\text{PO}_4$ powder or the post treatment by heating in non oxidising atmosphere takes place in the presence of at least one further component, in particular a carbon containing or electron conducting substance or the precursor of an electron conducting substance.
- 20 4. A process according to claim 1, wherein at least part of the $\text{Li}^{(\text{I})}$ is introduced as LiOH .
5. A process according to claim 1, wherein at least part of the $\text{P}^{(\text{V})}$ is introduced as H_3PO_4 .
- 25 6. A process according to claims 4 and 5, wherein the pH of the water-based mixture is obtained by adjusting the ratio of LiOH to H_3PO_4 .
7. Process according to any one of claims 1 to 6, characterised in that the atmospheric boiling point of the water-based mixture is between 100 and 150 °C, and preferably between 100 and 120 °C.

8. Process according to any one of claims 1 to 7, characterised in that the aprotic dipolar additive contained in the water-based mixture is dimethylsulfoxide.
9. Process according to any one of claims 2 to 8, characterised in that the step of post treatment of the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ is performed at a temperature of up to 675 °C, and preferably of at least 300 °C.
10. Process according to any one of claims 3 to 9 characterised in that the electron conducting substance is carbon, in particular conductive carbon or carbon fibres.
11. Process according to any one of claims 3 to 9 characterised in that the precursor of an electron conducting substance is a carbon conducting substance, in particular a polymer or sugar-type macromolecule.
12. A crystalline $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ powder with $0 < x < 1$, for use as electrode material in a battery, having a particle size distribution with an average particle size d_{50} of less than 100 nm, and preferably of more than 30 nm.
13. A $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ powder according to claim 12, characterised in that the maximum particle size is less than or equal to 500 nm.
14. A $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ powder according to claims 12 or 13, characterised in that the particle size distribution is mono-modal and in that the ratio $(d_{90} - d_{10}) / d_{50}$ is less than 1.5, preferably less than 1.3.
15. Composite powder containing a $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ powder according to any one of claims 12 to 14, and up to 10 %wt of a conductive additive.
16. Electrode mix containing the composite powder according to claim 15.

17. Use of the composite powder according to claim 15 for the manufacture of a lithium insertion-type electrode, by mixing said powder with a conductive carbon-bearing additive.
- 5 18. A crystalline $\text{LiFe}_{1-x}\text{Co}_x\text{PO}_4$ powder with $0 < x < 1$, for use as electrode material in a battery, having a particle size distribution with an average particle size d_{50} of less than 300 nm, and preferably of more than 30 nm.
- 10 19. A $\text{LiFe}_{1-x}\text{Co}_x\text{PO}_4$ powder according to claim 18, characterised in that the maximum particle size is less than or equal to 900 nm.
20. A $\text{LiFe}_{1-x}\text{Co}_x\text{PO}_4$ powder according to claims 18 or 19, characterised in that the particle size distribution is mono-modal and in that the ratio $(d_{90} - d_{10}) / d_{50}$ is less than 1.5, preferably less than 1.1.
- 15 21. Composite powder containing a $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ powder according to any one of claims 18 to 20, and up to 10 %wt of a conductive additive.
- 20 22. Electrode mix containing the composite powder according to claim 21.
23. Use of the composite powder according to claim 21 for the manufacture of a lithium insertion-type electrode, by mixing said powder with a conductive carbon-bearing additive.

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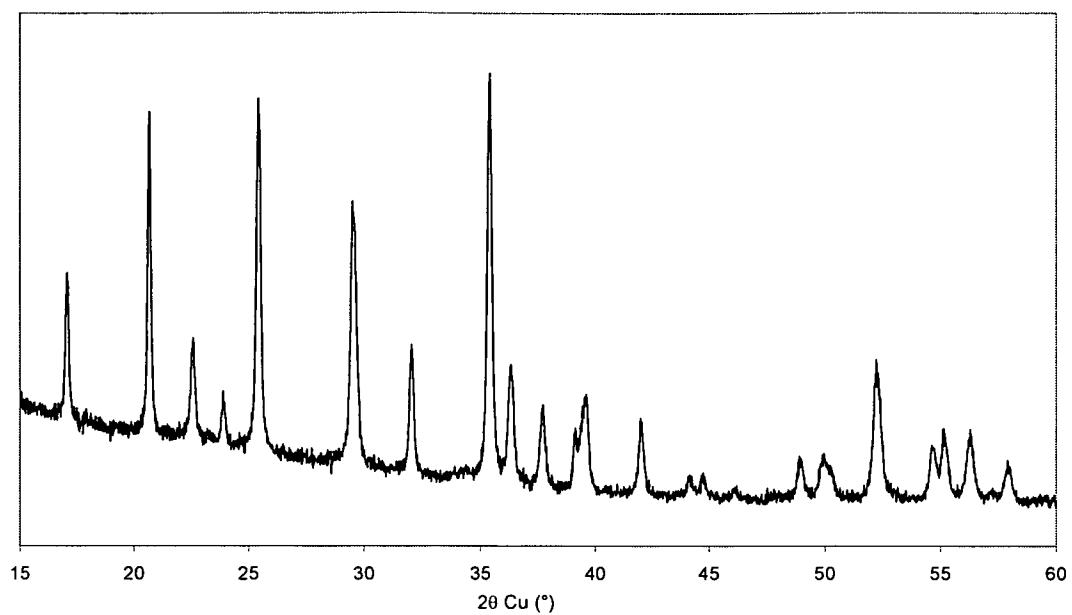


Fig. 1

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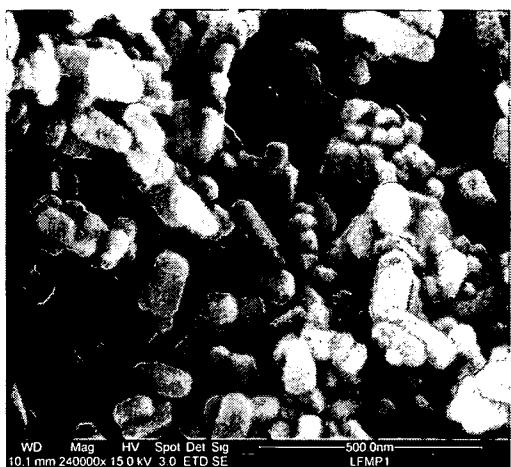


Fig. 2

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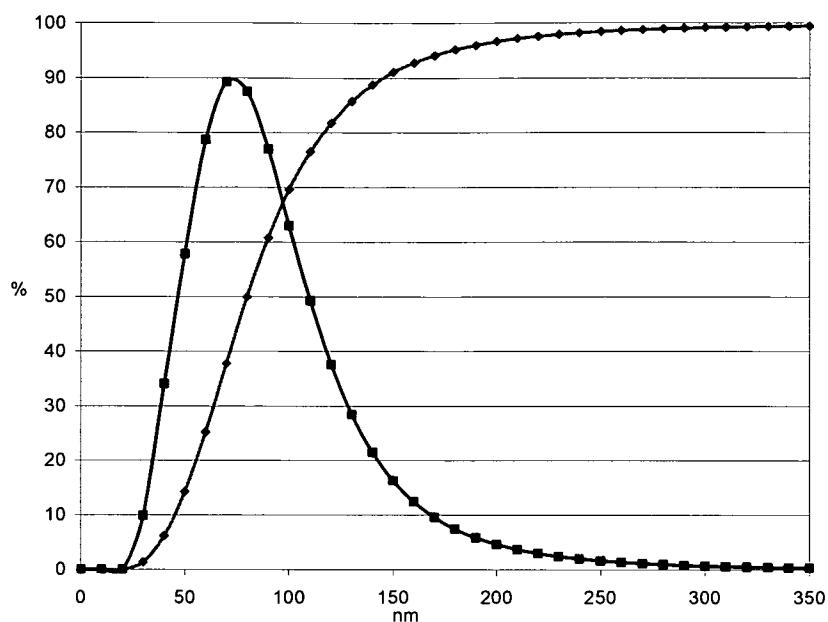


Fig. 3

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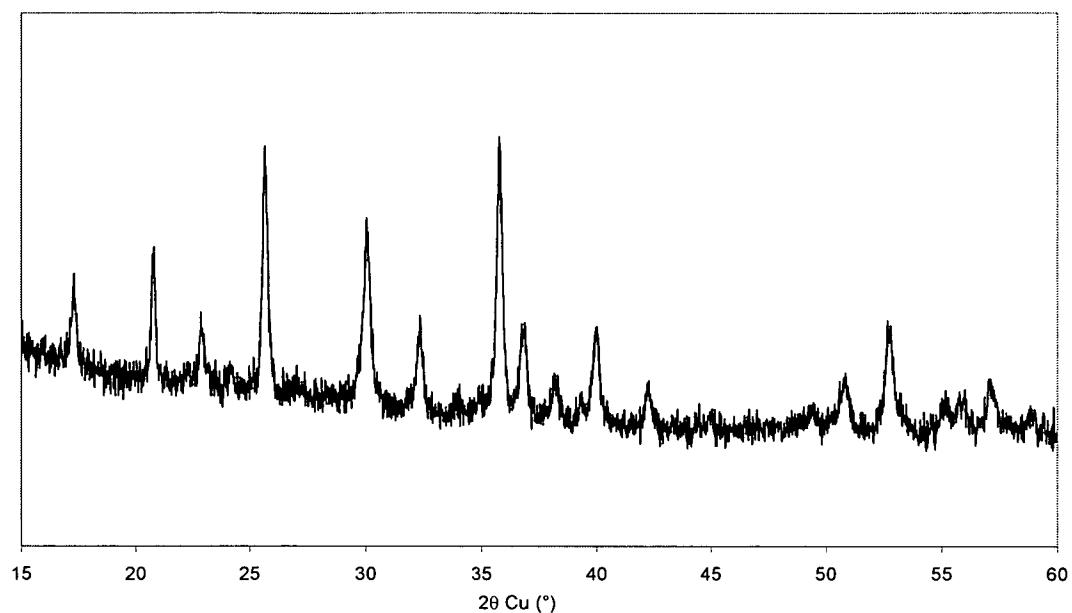


Fig. 4

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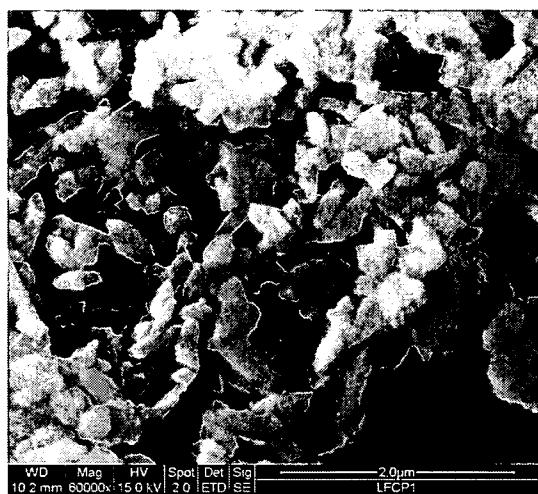


Fig. 5

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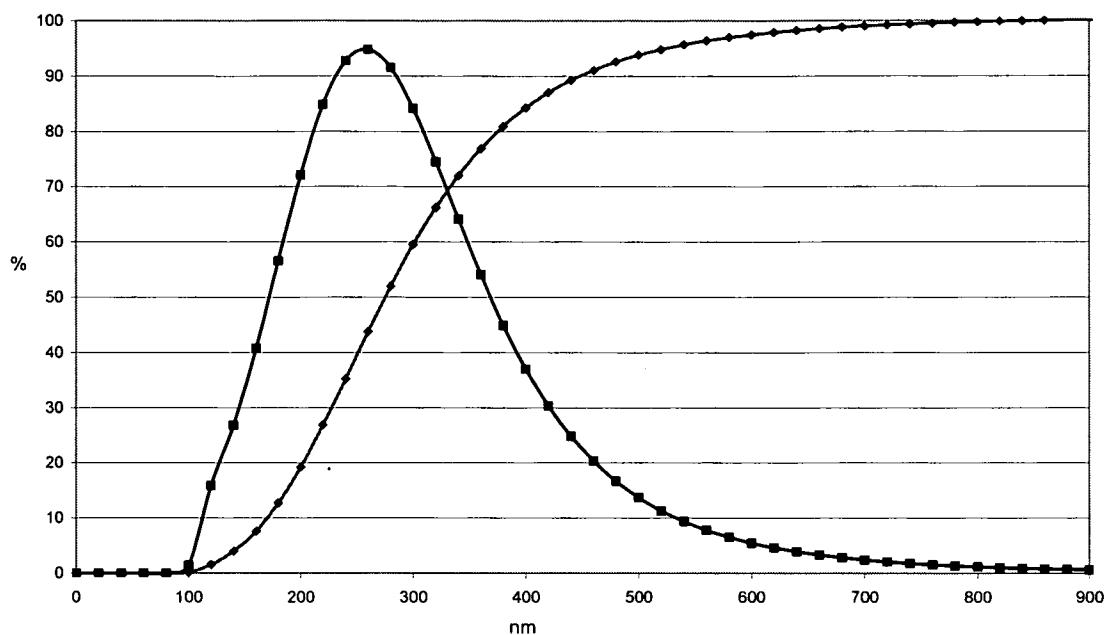


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/009969

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C01B25/30 C01B25/37 C01B25/45

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2006/105848 A (SUED CHEMIE AG [DE]; SCHALL NORBERT [DE]; NUSPL GERHARD [DE]; VOGLER C) 12 October 2006 (2006-10-12) page 11, line 28 - page 16, line 13 -----	1-23
A	WO 2005/051840 A (SUED CHEMIE AG [DE]; NUSPL GERHARD [DE]; WIMMER LUCIA [DE]; EISGRUBER) 9 June 2005 (2005-06-09) page 3, line 8 - page 19, line 10 -----	1-23
A	WO 02/099913 A (UMICORE S A NV [BE]; WURM CALIN [FR]; MORCRETTE MATHIEU [FR]; GWIZDALA) 12 December 2002 (2002-12-12) abstract ----- -/-	1-23

Further documents are listed in the continuation of Box C.

See patent family annex.

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Date of the actual completion of the international search

26. March 2008

Date of mailing of the International search report

14/04/2008

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 Fax: (+31-70) 340-3016

Authorized officer

Lecerf, Nicolas

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2007/009969

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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