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(54) **Title:** METHOD FOR PREPARING CARBON COATED ELECTRODE ACTIVE MATERIAL PARTICLES

(57) **Abstract:** The present invention is related to a method for preparing particles having a core made of an electrode active material, and a carbon coating Said method is based on a physical deposition of carbon, wherein the particles to be coated remain under dry conditions at a temperature lower than their decomposition temperature, during the whole process, hence avoiding all the drawbacks mentioned above and being generally applicable to all electrode active materials. Said method comprises the steps of: providing active material particles; coating said particles with a carbon film by a thermal vapor deposition (TVD) method using carbon as the carbon source; wherein the particles remain at a temperature lower than their decomposition temperature and under mechanical agitation during the coating process.

METHOD FOR PREPARING CARBON COATED ELECTRODE ACTIVE MATERIAL PARTICLES

The present invention is related to a method for preparing particles having a core made of an electrode active material, and a carbon coating.

5

BACKGROUND OF THE INVENTION

Batteries comprise a positive and a negative electrode which are electronically insulated from each other but in contact with an ionic conducting medium, the electrolyte. Except for metal electrodes (such as lithium anodes) electrodes are made of a metal current collector onto which a material is deposited
10 by different means, said material comprising an active material and preferably some additives, such as a binder to ensure mechanical strength and an electronic conducting agent (for instance carbon black). Still, active materials must exhibit high intrinsic electronic and ionic conductivities in order to have acceptable reaction kinetics and hence to be able to operate at the required intensities. The
15 higher the charge /discharge rates at which the battery is expected to operate, the larger electronic and ionic conductivities the electrodes must have.

Battery calendar life upon cycling is enhanced if side reactions, which result in slow degradation of the electrode/electrolyte interfaces, can be avoided. These energetically favored side reactions mostly involve charged electrode materials
20 reacting with nonaqueous electrolytes. [J.B. Goodenough, Y. Kim. Chem. Mater. 22 (2010) 587]

A common practice, especially for low intrinsic conductivity electrode materials, such as LiFePO_4 , is to coat the particles surface with a conducting compound which can be a metal, a conducting polymer or, most generally, carbon
25 [J. Wang, X. Sun, Energy & Environmental Science, 5 (2012) 5163]. Following this approach, the poor conductivity is alleviated by creating a conductive carbon coating layer on the active material particles with a minimal amount of adherent carbon (usually less than 2% in weight). [WO 02/27823 A1].

Furthermore, since carbon has a wide electrochemically stable window in
30 organic electrolytes and has good chemical stability, carbon coatings do also prevent surface degradation in electrode materials and hence slow down the capacity fading upon battery cycling [B.L. Cushing, J.B. Goodenough, Solid State Sciences 4 (2002) 1487]. Other advantages of carbon coating include promoting a more uniform SEI (Solid Electrolyte Interphase) layer [C. Natarajan, H. Fujimoto,
35 K. Tokumitsu, A. Mabuchi, T. Kasuh, Carbon 39 (2001) 1409] and buffering of

volume changes in active materials and hence circumventing the peeling-off of active material from the current collector due to cracking and pulverization [Y.J. Kwon, J. Cho, Chem. Commun 9 (2008) 1109].

Carbon coating on powdered active materials used for battery electrode
5 fabrication is currently achieved through chemical procedures [H. Li and, H. Zhou. Chem Commun. 48 (2012) 1201]: (i) Chemical/Thermal Vapor deposition using toluene, benzene or an alternative carbon source, (ii) *in situ* growth of the carbon coating layer during the materials synthesis thanks to the addition of a carbon source to the reacting medium (e.g sucrose, citric acid) or (iii) a post-synthetic
10 treatment involving either spray pyrolysis of a suspension containing the active material and a carbon source or mixing the powdered electrode active material with a carbon precursor using a liquid dispersing medium and performing thermolysis of the mixture in order to decompose the precursor into carbon at high temperatures (ca. 700°C), mostly under inert gas flow. These multi-step routes are of high cost
15 and energy consuming and may be difficult to upscale. The carbon yield (the efficiency of conversion of precursor into carbon) is difficult to estimate *a priori* since it is quite independent of the initial mass ratio between the active particle and carbon precursor [J. Moskon, R. Dominko, R. Cerc-Korosec, M.Gaberscek, J. Jamnik. J. Power Sources 174 (2007) 683].

20 These procedures can be applied to a large variety of materials either for the positive or negative electrode and aim at best at achieving a uniform particle shell on the particle powders, which remain at the core. However, they are not applicable for electrode active materials i) which may decompose under the high temperatures needed to decompose the carbon precursor to achieve carbon coating or ii) which
25 may be reduced under the thermal treatment conditions or for materials needing processing under oxidizing conditions which may lead to burn out of added organic precursors. If the electrode active material has a particle size in the nanometric range, the thermal treatment may also induce particle growth and/or agglomeration. Another drawback of such methods is the difficulty of coating materials that can
30 dissolve in the liquid used to prepare the dispersion which will further be thermally treated. Finally, the control of the thickness and uniformity of the carbon layer is also a challenge since it depends on a large amount of parameters: the precursor used, its weight ratio and the homogeneity of the mixture, particle size of the active material etc. While a low amount of carbon precursor may form a thin but hardly a
35 full coating layer on the particle surface, a too thick layer would act as a barrier for ion diffusion.

Alternatively, ball milling with carbon is also a generally used procedure to promote intimate mixture which sometimes results in enhanced electrochemical properties. In these cases, no continuous conductive film of carbon is achieved but rather a nanocomposite. This can be considered as a variant of the traditional
5 electrode preparation procedure where the active material is mixed with carbon black and a binder, rather than a technique to produce uniform carbon coating on particles.

Carbon evaporation under vacuum (around 10^{-2} Pa) from a pre-shaped carbon rod of a woven thread of carbon fiber is known to produce conductive
10 carbon coatings on samples to enable charge free imaging in electron microscopy and microprobe analysis, with a thickness of ca. 2 nm or more [K. Rüdiger-Peters. J. Microscopy 133 (1984) 17]. The technique was introduced by Bradley in the electron microscopy field and produces cohesive films covering even fissured surfaces [I.M. Watt. Cambridge University Press. (1997). ISBN-13: 978-
15 0521435918]. Commercial evaporators are manufactured to that end by various companies but never used to apply a uniform carbon coating on powdered electrode active material.

US-6 733 923 discloses a method for preparing an electrode, said method comprising a step of preparing a composite electrode material containing an oxide,
20 acetylene black as an electronic conducting agent and PVDF as a binder, a step of preparing a film of said composite material and a step of coating said film with carbon through different techniques for instance a heating deposition process. WO 2011/109457 also discloses a surface modified cathode and method of making surface modified cathode, said method comprising a step of coating the free surface
25 of active material particles at the upper surface of a cathode film or the surface of active material particles facing the upper surface of the cathode.

However, in an electrode obtained according to these methods, only the surface of the electrode or only the part of the surface of the particles facing the upper surface is in contact with the carbon coating and not the whole surface of
30 each individual particles, which remain partially uncoated, so the effect is only on the surface of the electrode but not on the bulk thereof.

In contrast, if each particle forming the electrode material was coated, thick (high energy density) electrodes with enhanced electronic conductivity could be manufactured, which would be suitable for battery operation at higher intensities
35 (higher power density).

THE INVENTION

The present invention intends to provide a method for the production of particles having an active material core and a carbon coating on the whole surface of each particles, said particles being then used to manufacture an electrode for a
5 battery.

Said method is particularly useful for coating particles of an active material that would be degraded at temperatures needed to decompose carbon precursors to yield carbon coating the particles, either because the intrinsic decomposition temperature of said active material is lower than the temperature required for the
10 pyrolytic decomposition of carbon precursor to yield carbon, or because said active material would be degraded under the conditions existing during the pyrolysis process such as the reducing atmosphere. Furthermore the method is particularly useful for particles of an active material that would dissolve in the solvent used for the traditional coating method involving a step where the carbon precursor is mixed
15 with the active material using a liquid dispersing medium prior to pyrolysis.

The method of the present invention is based on a physical deposition of carbon, wherein the particles to be coated remain under dry conditions at a temperature lower than their decomposition temperature, during the whole process, hence avoiding all the drawbacks mentioned above and being generally applicable
20 to all electrode active materials.

The method of the present invention comprises the steps of:

- providing active material particles;
- coating said particles with a carbon film by a physical vapor deposition (PVD) method using carbon as the carbon source;

25 wherein:

- the particles remain at a temperature lower than their decomposition temperature, and
- the physical vapor deposition is a thermal vapor deposition method (TVD) comprising at least the following steps:
30 i) an element made of carbon and surrounded by a metal filament, typically a tungsten filament, is present in a vacuum chamber;
ii) an active material in powder form is placed on a support in the vacuum chamber;
iii) the powder is agitated by mechanical means;

- iv) the vacuum chamber is put under vacuum at a pressure lower than 10^{-1} Pa (10^{-3} mbar), more preferably lower than 10^{-2} Pa (10^{-3} mbar);
- v) a current is applied to the tungsten filament to heat the carbon and generate carbon vapor in the chamber.

5 With respect to methods currently used, mostly based on pyrolysis of carbon precursors, the method of the invention has the following advantages: it avoids heating the active material, it avoids submitting the active material to reducing conditions while hot and it avoids processing the active material in liquid medium. Thus, it is specially suited to thermally unstable materials, materials containing
10 transition metals in high oxidation states which would be reduced during the pyrolysis of carbon precursors or materials reacting with liquids which cannot be coated by chemical means. Moreover, since there is no thermal treatment, particle growth is prevented and control of the amount of carbon (i.e. the thickness of the coating layer) is easy through control of deposition time. Furthermore, as the
15 method is implemented at low temperature, the cost thereof is lower. Finally, as the coating is carried out under continuous mechanical agitation, all the sides of the particles are exposed to carbon and hence the claimed process leads to a coating of the whole surface of each individualized particles.

Although the method of the invention is particularly useful to prepare carbon
20 coated particles having a core made of an active electrode material that is thermally unstable, it may be carried out to prepare carbon coated particles from all types of active materials generally used for either the cathode or the anode of various batteries, in particular for a lithium battery.

Detailed description of the preferred embodiments

25 The method of the invention is particularly useful for the preparation of electrode active materials that have low thermal stability and/or that may react with solvents.

Active cathode materials may be selected from:

- transition metal oxides having spinel or layered type structures such as
30 $\text{Li}_{1+x}\text{M}_{2-x}\text{O}_4$ with $0 \leq x \leq 0.3$ or $\text{A}_{1+x}\text{M}_{1-x}\text{O}_2$, with $0 \leq x \leq 0.3$; or
- oxides exhibiting a polyanionic framework with formula $\text{A}_y\text{M}(\text{XO}_4)_z\text{F}_t$ with $0 \leq y \leq 2$, $1 \leq z \leq 1.5$, $0 \leq t \leq 1$;
- lead sulphate
- $\text{Ni}_{1-x}\text{M}'_x(\text{OH})_2$ where M' is transition metal

where M is selected from Mn, Fe, Co, Ni, Cu, V, Ti, Mg, Al, Zn or a mixture of them, X is selected from S, P, or Si and A is either Na or Li.

Examples of active cathode materials that are unstable at temperatures required for coating methods involving pyrolysis of an organic carbon precursor are: nickel oxihydroxides or hydroxides as $\text{Ni}_{1-x}\text{M}_x(\text{OH})_2$ where M can be any transition metal, and lead sulphate.

Examples of active cathode materials that are unstable because they would degrade within the reducing atmosphere existing during the pyrolysis of an organic carbon precursor are layered $\text{A}_{1+x}\text{M}_{1-x}\text{O}_2$ materials with $0 \leq x \leq 0.3$ where M is a transition metal in high oxidation state. Examples are $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.5}\text{Ni}_{0.15}\text{Co}_{0.15}\text{O}_2]$, FePO_4 or any other compound containing Fe^{3+} such as FeSO_4F , and LiCoPO_4 .

LiCoPO_4 exhibits the same olivine structure as LiFePO_4 and an operation voltage that is 1.4 V higher than that of LiFePO_4 , but its electronic conductivity is much lower than that of LiFePO_4 and thus carbon coating is necessary. However, cobalt compounds being effective catalysts in the carbon gasification processes, the achievement of a coating through a process involving high temperature treatment is much more difficult since the added carbon can be consumed, causing reduction of LiCoPO_4 at the surface of the particles to Co_2P [J. Wolfenstine, J. Read, J.L. Allen. J. Power Sources 163 (2007) 1070].

Active cathode material that would dissolve or react with a solvent are LiFeSO_4F and lithium or sodium transition metal fluorides where transition metal is iron, manganese or vanadium.

A typical example is MFeSO_4F (M=Li, Na or a mixture of both). LiFeSO_4F exhibits interesting performances as positive electrode material for lithium ion batteries with reversible capacities around 140mAh/g at 3.6V vs. $\text{Li}^+/\text{Li}^\circ$. [N. Recham, J.N. Chotard, L. Dupont, C. Delacourt, W. Walker, M. Armand, J.M. Tarascon. Nat. Mater. 9 (2010) 68], [WO2010046610 A1]. However, LiFeSO_4F is not stable at temperature higher than 350°C, which prevents any attempt of performing carbon coating on it by the usual methods involving higher temperatures to promote decomposition of the carbon precursors. Moreover, the compound cannot be processed in aqueous medium since it decomposes to yield FeOOH and LiF .

Active materials useful for an anode are preferably selected from silicon, tin, carbon, graphite, lithium titanium oxide, lithium vanadium oxide, sodium titanium oxide, sodium vanadium oxide, titanium oxide, cobalt oxide, iron oxide, copper oxide, nickel oxide, iron fluoride, lead sulphate or an organic electrode material.

Active anode materials having a low decomposition temperature are lead sulphate and any organic electrode material [Y. Liang, Z. Tao, J. Chen. *Advanced Energy Materials* 2 (2012) 742] such as organosulfur compounds (RSSR where R can be any organic moiety) or organosulfur polymers containing disulfide or polysulfide bonds; organic free radical compounds, such as nitroxide-based polymers; or carbonyl compounds like sodium terephthalate, or lithium or sodium rhodizionate.

Active anode materials that are unstable because they would degrade within the reducing atmosphere existing during the pyrolysis of an organic carbon precursor are transition metal oxides such as Fe_2O_3 or Co_3O_4 [B. V. L'vov, *Thermochim. Acta*, 360 (2000) 109].

Active anode material that would dissolve or react in a solvent are organic electrode materials, sodium titanium oxide, sodium vanadium oxide.

The particle size of the active material is preferably in the range between 5 nm and 700 μm .

The carbon coating on the active material core of the carbon coated particles has preferably a thickness in the range of 1 to 20 nm.

According to the thermal vapor deposition method of the invention, when carbon vapor generated in the vacuum chamber is in contact with the surface of the powder particles which are at ambient temperature, carbon is deposited on the whole surface of the particles.

The deposition rate is regulated by means of the current applied and the thickness of the deposit depends on the deposition time. A higher current applied provides a higher deposition rate. A longer deposition time provides a thicker coating.

The deposition rate is preferably in the range of 0.05 to 0.4 nm/s. Deposition time can be varied allowing a direct control on the coating thickness. A deposition time in the range of 1 minute to 2 hours provides generally an efficient coating thickness.

The amount of active material particles put in the vacuum chamber depends on the size of said vacuum chamber.

The size of the active material particles is preferably in the range of 5 nm to 700 micrometers.

The carbon source is preferably a carbon rod or a woven thread of carbon fiber.

Figure 1 is a high resolution transmission microscopy image of carbon coated LiFeSO_4F particles.

Figure 2 is the X-ray diffraction pattern for the carbon coated LiFeSO_4F (curve C) and uncoated LiFeSO_4F (curve U), respectively.

5 Figures 3a and 3b are Mössbauer spectra for the uncoated LiFeSO_4F and the carbon coated LiFeSO_4F , respectively. T is the transmission and V is the velocity (in mm/s). The curves represented by $\circ\circ\circ\circ\circ$ and — correspond to the experimental data and to the calculated data, respectively. The calculated data result from the addition of contributions for the Fe^{2+} (1) and Fe^{2+} (2) crystallographic sites of Fe^{2+} in the LiFeSO_4F tavorite structure represented by - - -
10 - - - - and — , respectively.

Figure 4 represents the Raman spectrum for carbon coated LiFeSO_4F powder. RI is the Raman Intensity (in counts/s) and RS is the Raman shift (in cm^{-1}). The curves represented by $\circ\circ\circ\circ\circ$ and — correspond to the experimental and
15 data and to the calculated data, respectively. The calculated data result from the contribution of the D and G bands of carbon represented by - - - - - and — , respectively.

Figure 5 shows first cycle Potential (P, in V vs Li^+/Li) versus capacity (C, in mAhg^{-1}) profiles for tape electrodes prepared with coated LiFeSO_4F (curve
20 $\square-\square-\square-\square-\square-\square-\square-\square$) and for tape electrodes prepared with uncoated LiFeSO_4F (curve $\blacktriangle-\blacktriangle-\blacktriangle-\blacktriangle-$), both cycled in 1M LiBOB in EC electrolyte at 100°C with a lithium metal counter electrode in Swagelok type cells.

Figure 6 represents the specific current density I (mAhg^{-1}) versus Potential P (V vs Li^+/Li) for tape electrodes prepared with carbon coated LiFeSO_4F (curve
25 $\square-\square-\square-\square-\square-\square-\square-\square$) and for tape electrodes prepared with uncoated LiFeSO_4F (curve $\blacktriangle-\blacktriangle-\blacktriangle-\blacktriangle-$), both cycled in 1M LiBOB in EC electrolyte at 100°C with a lithium metal counter electrode in Swagelok type cells. Sweep rate is 1mVs^{-1} .

Figure 7 is an expanded view of Figure 6.

Figure 8 represents the Nyquist plots with the imaginary (I) versus the real
30 components (R) of the impedance, plotted for various frequencies (ranging from 500 kHz to 50 mHz) for powder electrodes prepared with carbon coated ($\square\square\square\square\square\square\square$) and for powder electrodes prepared with uncoated ($\blacktriangle\blacktriangle\blacktriangle\blacktriangle$) LiFeSO_4F . Electrochemical impedance spectroscopy measurements were performed in 3 electrode Swagelok cells at room temperature using LP30
35 electrolyte and lithium metal counter and reference electrodes.

Figure 9 is a high resolution transmission microscopy image of carbon coated LiCoPO₄.

Figure 10 shows first cycle Potential (P, in V vs Li⁺/Li) versus capacity (C, in mAhg⁻¹) profiles for tape electrodes prepared with coated LiCoPO₄ (curve $\square-\square-\square-\square-\square-\square-\square-\square$) and for tape electrodes prepared with uncoated LiCoPO₄ (curve $\blacktriangle-\blacktriangle-\blacktriangle-\blacktriangle-$), both cycled in LP30 electrolyte at room temperature with a lithium metal counter electrode in Swagelok type cells.

Figure 11 represents a) the Coulombic efficiency CE (in %) and b) the capacity retention CR (%) versus the number of cycles N for tape electrodes prepared with carbon coated LiCoPO₄ ($\square\square\square\square\square\square\square$) and for tape electrodes prepared with uncoated LiCoPO₄ ($\blacktriangle\blacktriangle\blacktriangle\blacktriangle$) cycled in LP30 electrolyte at room temperature with a lithium metal counter electrode in Swagelok type cells.

Figure 12 shows high resolution transmission microscopy images of carbon coated Co₃O₄ nanoparticles with (a) 5 minutes, (b) 15 minutes and (c) 30 minutes deposition time.

Figure 13a) shows first cycle Potential (P, in V vs Li⁺/Li) versus capacity (C, in mAhg⁻¹) profiles for tape electrodes prepared with coated Co₃O₄ (deposition time is 5 minutes, curve $\square-\square-\square-\square-\square-\square-\square-\square$) and for tape electrodes prepared with uncoated Co₃O₄ (curve $\blacktriangle-\blacktriangle-\blacktriangle-\blacktriangle-$) cycled in LP30 at room temperature with a lithium metal counter electrode in Swagelok type cells. Fig.13b) displays the normalized voltage versus capacity profiles at the end of the first discharge for same experiments.

Figure 14 represents the capacity (C, in mAhg⁻¹) versus the number of cycles N for tape electrodes prepared with carbon coated Co₃O₄ ($\square\square\square\square\square\square\square$) with 5 minutes deposition time and for tape electrodes prepared with uncoated Co₃O₄ ($\blacktriangle\blacktriangle\blacktriangle\blacktriangle$), both cycled in LP30 at room temperature with a lithium metal counter electrode in Swagelok type cells.

Figure 15 shows a picture of Li₄Ti₅O₁₂ powder (a) uncoated, and of carbon coated Li₄Ti₅O₁₂ powder after a deposition time of 10 minutes (b), 20 minutes (c) and 30 minutes (d).

Figure 16 is a high resolution transmission microscopy image of carbon coated Li₄Ti₅O₁₂.

Figure 17 shows the Potential (P, in V vs Li⁺/Li) versus capacity (C, in mAhg⁻¹) profiles for tape electrodes prepared with a) coated Li₄Ti₅O₁₂ and for tape electrodes prepared with b) uncoated Li₄Ti₅O₁₂ both cycled in LP30 at room temperature at rates ranging from C/5 to 8C.

Figure 18 represents the capacity (C, in mAhg^{-1}) versus the number of cycles (N) for tape electrodes prepared with carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\square\square\square\square\square\square$) and for tape electrodes prepared with uncoated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\blacktriangle\blacktriangle\blacktriangle\blacktriangle$), both cycled in LP30 at room temperature with a lithium metal counter electrode in Swagelok type cells.

5 Figure 19 is a high resolution transmission microscopy image of carbon coated sodium rhodizonate particles.

Figure 20 is a high resolution transmission microscopy image of carbon coated Sn particles.

10 Figure 21 is a high resolution transmission microscopy image of carbon coated Si particles.

Figure 22 shows first cycle Potential (P, in V vs Na^+/Na) versus capacity (C, in mAhg^{-1}) profiles for tape electrodes prepared with coated hard carbon (deposition time is 30 minutes, curve $-\square-\square-\square-\square-\square-\square-\square-\square$) and for tape electrodes prepared with uncoated hard carbon (curve $\blacktriangle-\blacktriangle-\blacktriangle-\blacktriangle-$) cycled in 15 1M NaClO_4 in $\text{EC}_{0.45}:\text{PC}_{0.45}:\text{DMC}_{0.1}$ at room temperature with a sodium metal counter electrode in Swagelok type cells.

Figure 23 is a high resolution transmission microscopy image of carbon coated $\text{Ni}(\text{OH})_2$ particles.

20 Figure 24 is a high resolution transmission microscopy image of carbon coated $\text{Na}_2\text{Ti}_3\text{O}_7$ particles.

Figure 25 is a high resolution transmission microscopy image of carbon coated LiFePO_4 particles.

EXAMPLES

The products used in the examples are:

25 PVDF	polyvinylidene fluoride, provided by Arkema
Csp	Super P carbon, provided by Timcal
NMP	N-methylpyrrolidone, provided by Sigma-Aldrich
Al foil	a 20 μm thick aluminum foil provided by Goodfellow
Li foil	a lithium foil provided by Chemetall
30 Whattman GF/d	a borosilicate glass fiber provided by Whattman
LP30	a 1M LiPF_6 in $\text{EC}:\text{DMC}$ 1:1 electrolyte provided by Merck
LiBOB	Lithium bis(oxalato)borate by Chemetall
EC	ethylene carbonate provided by Sigma-Aldrich

LiCoPO ₄	provided by Sigma-Aldrich
Co ₃ O ₄	provided by Sigma-Aldrich
Li ₄ Ti ₅ O ₁₂	provided by Sigma-Aldrich
Sodium rhodizionate	provided by Sigma-Aldrich
5 Sn	provided by Sigma-Aldrich
Si	provided by Sigma-Aldrich

LiFeSO₄F is prepared as by ionothermal synthesis starting from FeSO₄ · H₂O and LiF as described in N. Recham, J.N. Chotard, L. Dupont, C. Delacourt, W. Walker, M. Armand, J.M. Tarascon. *Nat. Mat.* 9 (2010) 68.

10 Hard C is prepared by pyrolysis of sugar as described in A. Ponrouch, E. Marchante, M. Courty, J.M. Tarascon, M. R. Palacín. *Energy&Environmental Science* 2012, 5, 8572-83.

Ni(OH)₂ is prepared by direct precipitation after mixing a 1M solution of nickel sulphate hexahydrate and 2M solution of sodium hydroxide as described in
15 M. Casas-Cabanas, J. Rodríguez-Carvajal, J. Canales-Vázquez, M.R. Palacín. *J. Mater. Chem.* 2006, 16, 2925-2939.

Na₂Ti₃O₇ is prepared by solid state reaction between TiO₂ and Na₂CO₃ at 800°C as described in P. Senguttuvan, G. Rouse, V. Seznec, J.M. Tarascon, M.R. Palacín. *Chem. Mater.*, 2011, 23, 4109.

20 LiFePO₄ is prepared by solid state reaction between LiH₂PO₄ and FeC₂O₄ · 2H₂O by two successive thermal treatments at 350 and 800°C as described in S.S Zhang, J.L Allen, K Xu, T.R Jow, *J. Power Sources*, 2005, 147, 234.

In each example, the coated particles were prepared using a high vacuum coating system provided under the trade name Bal-Tec Med 020, by Leica
25 Microsystems. Said device comprises a clean high-vacuum pump in combination with a removable vacuum chamber, rotary-planetary-tilting sample holder and quartz crystal film thickness monitor system. A system allowing continuous mechanical agitation of the particles during the coating process has been added, said system consisting of a spatula fixed to the deposition chamber in direct contact
30 with the rotary-planetary-tilting sample holder. The deposition rate was measured through a quartz crystal film inside the vacuum chamber and hence was directly read.

Example 1

Carbon coated LiFeSO₄F

Preparation of the carbon coated particles

Carbon coated LiFeSO₄F was prepared using the above mentioned Bal-Tec
5 Med 020 coating system.

An amount of 600 mg of LiFeSO₄F having a particle sizes ranging from 50
to 400 nm was put in the vacuum chamber. The carbon source in the vacuum
chamber was a carbon rod, the pressure in the vacuum chamber was about 10⁻² Pa
(10⁻⁴ mbar). The deposition time was around 2 hours. The deposition rate was
10 around 0.1 nm/s.

The high resolution transmission microscopy represented on figure 1 shows
that the resulting carbon coated particles have a uniform coating of about 20 nm.

Mössbauer spectroscopy and X-ray diffraction

Mössbauer spectroscopy and X-ray diffraction analysis were performed
15 before and after carbon coating. They indicate that neither the structure nor the
oxidation state of iron in the compound are modified by the carbon coating process.
The iron XRD pattern (represented on figure 2) does not change and the Mössbauer
spectra (represented on figure 3) are identical. The Mössbauer spectra were fitted
with two doublets in accordance with the two crystallographic sites of Fe²⁺ in the
20 favorite LiFeSO₄F structure and the Mössbauer parameters are identical to those
already reported for that phase. No trace of Fe³⁺ is detected.

The Raman spectrum (represented on figure 4) for carbon coated LiFeSO₄F
powder exhibits two broad bands at 1350 and 1580 cm⁻¹ (D and G bands of
carbon). The ratio between them allows evaluating the degree of disorder in the
25 carbon as previously reported for carbon coated LiFePO₄. [M. M. Doeff, Y. Hu, F.
Mc Larnon, R. Kostecki, Electrochem. Solid-State Lett. 6 (2003) A207], for which
a D/G ratio of ca. 2 or lower has been found to be optimum. In this case, a D/G
bands ratio of ca. 1.5 was calculated from figure 4, indicating a high degree of
graphitization of the carbon coated layer and thus high electronic conductivity.

Preparation of "tape" electrodes

Slurries were prepared by mixing 80wt.% of the active material with or
without carbon coating, 5wt.% of PVDF as a binder and 15wt.% of Csp as carbon
additive in NMP. Mixing of the slurries was performed by magnetic stirring during
3 h, the vial containing the slurry being placed in an ultrasonic bath for 10 minutes
35 every 1 h.

Composite electrodes were prepared by depositing the slurry on a 20 μm thick aluminum foil with a 250 μm Doctor-Blade and further dried at 120 $^{\circ}\text{C}$ under vacuum. Once dried, 0.8 cm^2 disk electrodes were cut and pressed at $7.8 \cdot 10^8$ Pa.

Electrochemical testing

5 "Tape" electrodes were tested in Swagelok type cells [D. Guyomard, J.M. Tarascon. J. Electrochem. Soc. 139 (1992) 937] with a disk of Li metal foil as counter electrode. Two sheets of Whatman GF/d borosilicate glass fiber were used as a separator, soaked with the electrolyte (ca. 0.5 cm^3 of 1M LiBOB in ethylene carbonate (EC). Electrochemical experiments were made at 100 $^{\circ}\text{C}$ to promote
10 electrolyte decomposition and better evaluate the impact of carbon coating reactivity of the active material with the electrolyte. These experiments were done in galvanostatic mode with potential limitation (GCPL) at a C/20 rate, meaning one mol of Li^+ per mol of LiFeSO_4F inserted in 20 hours. Almost full theoretical capacity (i.e. 151 mAhg^{-1}) is obtained in both cases for first oxidation (see figure
15 5). Better coulombic efficiency (difference of capacity recorded between the discharge and charge) is achieved in the case of carbon coated LiFeSO_4F with ca. 73.5% compared to 65.7% for uncoated LiFeSO_4F .

Cyclic voltamperometry at 1 mVs^{-1} was also performed. Significant oxidation current is measured above 4 V vs Li^+/Li in both cases due to the
20 electrolyte decomposition at the interface with the active material (cf. figure 6). The current intensity for such decomposition is decreased for carbon coated LiFeSO_4F and the onset potential significantly shifted to higher values, being observed at 4.31V for carbon coated LiFeSO_4F and at 4.18V for uncoated LiFeSO_4F (cf. figure 7). These results confirms the full coverage of LiFeSO_4F
25 particles by carbon coating.

Preparation of powder type electrodes and electrochemical impedance

Powder type electrodes were prepared by simple mixing the carbon coated LiFeSO_4F with Csp in a weight ratio of 80/20, in an agate mortar for 15 min.

Said electrodes (typical loading ca. 7 ± 1 mg) were used for electrochemical
30 impedance tests at room temperature in three electrode Swagelok type cells with a disk of Li metal foil as counter and reference electrodes. Two sheets of Whatman GF/d borosilicate glass fiber were used as a separator, soaked with the electrolyte (ca. 0.5 cm^3 of LP30). The charge transfer resistance in the carbon coated sample appeared to be significantly reduced, demonstrating the improved electronic
35 conductivity of the carbon coated particles compared with the uncoated particles (cf. figure 8).

Example 2

Carbon coated LiCoPO₄

Preparation of carbon coated particles

Carbon coated LiCoPO₄ were prepared according to the method described in example 1, using 600 mg of LiCoPO₄ having a particle sizes ranging from 100 nm to 1 μm, and a deposition time of around 30 minutes

The resulting carbon coated particles have a uniform coating of about 5 nm, as shown on figure 9. A gradual change in coloration was observed upon carbon deposition from purple for the uncoated powder to grey for the coated sample.

10 Preparation of "tape" electrodes

Tape electrode were prepared using the coated and the uncoated LiCoPO₄ particles according to method described in Example 1.

Electrochemical testing

"Tape" electrodes were tested in Swagelok type cells with a disk of Li metal foil as counter electrode. Two sheets of Whatman GF/d borosilicate glass fiber were used as a separator, soaked with the electrolyte (ca. 0.5 cm³ LP30) at room temperature. These experiments were done in galvanostatic mode with potential limitation (GCPL) at a C/20 rate, meaning one mol of Li⁺ per mol of LiCoPO₄ inserted in 20 hours.

20 High capacity is observed upon first oxidation (ca. about 120 mAhg⁻¹) for both coated and uncoated LiCoPO₄ (cf figure 10). Higher coulombic efficiency (58.2%) is achieved for carbon coated LiCoPO₄ when compared to uncoated LiCoPO₄ (46.8%). Better capacity retention upon cycling is also observed for the former (cf. figure 11).

25

Example 3

Carbon coated Co₃O₄

Preparation of carbon coated particles

Carbon coated Co₃O₄ were prepared according to the method described in example 1, using 600 mg of Co₃O₄ having a particle sizes ranging from 30 to 30 40 nm.

Transmission electron microscopy images taken on samples after 5, 15 and 30 min deposition time are given in figure 12. They show the evolution of the deposit thickness, which correspond respectively to 1, 2 and 4 nm.

Preparation of "tape" electrodes

Slurries were prepared by mixing 65wt.% of the active material with or without carbon coating, 8wt.% of PVDF as a binder and 27wt.% of Csp as carbon additive in NMP. Mixing of the slurries was performed by magnetic stirring during
5 3 h, the vial containing the slurry being placed in an ultrasonic bath for 10 minutes every 1 h.

Composite electrodes were prepared by depositing the slurry on a 20 μm thick copper foil with a 250 μm Doctor-Blade and further dried at 120 $^{\circ}\text{C}$ under vacuum. Once dried, 0.8 cm^2 disk electrodes were cut and pressed at $7.8 \cdot 10^8$ Pa.

10 Electrochemical testing

"Tape" electrodes were tested in Swagelok type cells with a disk of Li metal foil as counter electrode. Two sheets of Whatman GF/d borosilicate glass fiber were used as a separator, soaked with the electrolyte (ca. 0.5 cm^3 LP30) at room temperature. These experiments were done in galvanostatic mode with potential
15 limitation (GCPL) with a succession of 10 cycles at different C rates. First, 10 cycles were performed at C/5 followed by 10 cycles at C, C/5, 2C and finally C/5. Results are shown on figures 13 and 14.

The first cycle for both carbon coated and uncoated Co_3O_4 are very similar in terms of capacity, coulombic efficiencies and voltage hysteresis (cf. figure 13a).
20 However, the electrode prepared with carbon coated Co_3O_4 exhibits lower overpotential between discharge and charge at the end of the first reduction (cf. figure 13b). This is in agreement with the conductivity of carbon coated particles higher than the conductivity of the uncoated particles. A much better capacity retention is observed for carbon coated Co_3O_4 with a stable capacity of about ca.
25 1200 mAhg^{-1} achieved at C/5 after 90 cycles (cf. figure 14). Very good capacity retention is also observed at higher rates for carbon coated Co_3O_4 with capacities higher than 700 mAhg^{-1} at 2C, compared to only 300 mAhg^{-1} for uncoated Co_3O_4 . Since the non-uniform growth of a gel like film upon cycling, limits the diffusion of Li^+ within the electrode and induces capacity fade in electrodes prepared using
30 Co_3O_4 nanoparticles as active materials [A. Ponrouch and M.R. Palacín, J. Power Sources, 212 (2012) 233], it is straightforward to conclude that carbon coating on Co_3O_4 nanoparticles allows the growth of more uniform gel like film and therefore a better diffusion of Li^+ through the bulk of the electrode.

Example 4

Carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared according to the method of example 1. An amount of 600 mg of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ having a particle sizes ranging from 10 to 100 nm was put in the vacuum chamber. The carbon source in the vacuum chamber was a carbon rod, the pressure in the vacuum chamber was about 10^{-2} Pa (10^{-4} mbar). The deposition rate was around 0.1 nm/s.

A gradual change in coloration was observed upon carbon deposition from white for the uncoated powder to grey for the coated sample. Figure 15 shows the change of color from uncoated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder (a), and of carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder after a deposition time of 10 minutes (b), 20 minutes (c) and 30 minutes (d). After 30 minutes deposition time, the resulting carbon coated particles have a uniform coating of about 4 nm, as shown on figure 16.

Preparation of "tape" electrodes

Slurries were prepared by mixing 65wt.% of the active material with or without carbon coating, 8wt.% of PVDF as a binder and 27wt.% of Csp as carbon additive in NMP. Each slurry was mixed by magnetic stirring during 3 h, the vial containing the slurry being placed in an ultrasonic bath for 10 minutes every 1 h.

Composite electrodes were prepared by depositing the slurry on a 20 μm thick copper foil with a 250 μm Doctor-Blade and further dried at 120 $^{\circ}\text{C}$ under vacuum. Once dried, 0.8 cm^2 disk electrodes were cut and pressed at $7.8 \cdot 10^8$ Pa.

Electrochemical testing

"Tape" electrodes were tested in Swagelok type cells with a disk of Li metal foil as counter electrode. Two sheets of Whatman GF/d borosilicate glass fiber were used as a separator, soaked with the electrolyte (ca. 0.5 cm^3 LP30) at room temperature. These experiments were done in galvanostatic mode with potential limitation (GCPL) with a succession of 6 cycles at different C rates. First, 6 cycles were performed at C/5 followed by 10 cycles at C, C/5, 2C, C/5, 5C, C/5, 8C and finally C/5. Results are shown on figure 17 and 18.

The first cycle for both electrodes appeared to be very similar in terms of capacity, coulombic efficiencies and voltage hysteresis (cf. figure 17) for coated and uncoated $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The voltage hysteresis between charge and discharge at high C rates is much lower for carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in agreement with higher electronic conductivity. Upon cycling a much better capacity retention is observed for carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with a stable capacity of about ca. 155 mAhg^{-1} achieved at C/5 compared to only 140 mAhg^{-1} for uncoated $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Very good

capacity retention at high C rates is also achieved for carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with capacities higher than 135 mAhg^{-1} obtained at 8C compared to 120 mAhg^{-1} for uncoated $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Example 5

5 **Carbon coated sodium rhodizonate**

Preparation of carbon coated particles

Carbon coated sodium rhodizonate was prepared according to the method described in example 1, using 600 mg of sodium rhodizonate having a particle size ranging from 500 nm to $10\mu\text{m}$, and a deposition time of around 30 minutes.

10 The resulting carbon coated particles have a uniform coating of about 3 nm, as shown on figure 19. A gradual change in coloration was observed upon carbon deposition from dark green for the uncoated powder to dark grey for the coated sample.

Example 6

15 **Carbon coated Sn**

Preparation of carbon coated particles

Carbon coated Sn was prepared according to the method described in example 1, using 600 mg of Sn having a particle size ranging from 30 nm to 500 nm, and a deposition time of around 30 minutes.

20 The resulting carbon coated particles have a uniform coating of about 3 nm, as shown on figure 20.

Example 7

Carbon coated Si

Preparation of carbon coated particles

25 Carbon coated Si was prepared according to the method described in example 1, using 600 mg of Si having a particle size ranging from 200 nm to $5\mu\text{m}$, and a deposition time of around 30 minutes.

The resulting carbon coated particles have a uniform coating of about 4 nm, as shown on figure 21.

Example 8

Carbon coated hard carbon

Preparation of carbon coated particles

Carbon coated hard carbon was prepared according to the method described
5 in example 1, using 600 mg of hard carbon having a particle size ranging from 1 to
500 μ m, and a deposition time of around 30 minutes.

Preparation of "tape" electrodes

Tape electrode were prepared using the coated and the uncoated hard carbon
particles according to method described in Example 1.

10 Electrochemical testing

"Tape" electrodes were tested in Swagelok type cells with a disk of Na metal
foil as counter electrode. Two sheets of Whatman GF/d borosilicate glass fiber
were used as a separator, soaked with the electrolyte (ca. 0.5 cm³ 1M NaClO₄ in
EC_{0.45}:PC_{0.45}:DMC_{0.1}) at room temperature. These experiments were done in
15 galvanostatic mode with potential limitation (GCPL) at a rate equivalent to one mol
of Na⁺ per six moles of hard carbon inserted in 10 hours.

High capacity is observed upon first reduction (ca. about 500 mAhg⁻¹) for
both coated and uncoated hard carbon (cf figure 22) but higher coulombic
efficiency (70%) is achieved for carbon coated hard carbon when compared to
20 uncoated hard carbon (60%) in agreement with the coating diminishing electrolyte
decomposition.

Example 9

Carbon coated Ni(OH)₂

Preparation of carbon coated particles

25 Carbon coated Ni(OH)₂ was prepared according to the method described in
example 1, using 600 mg of Ni(OH)₂ having a particle size ranging from 10 nm to
200 nm, and a deposition time of around 1 hour.

The resulting carbon coated particles have a uniform coating of about 8 nm,
as shown on figure 23.

Example 10
Carbon coated Na₂Ti₃O₇

Preparation of carbon coated particles

Carbon coated Na₂Ti₃O₇ was prepared according to the method described in
5 example 1, using 600 mg of Na₂Ti₃O₇ having a particle size ranging from 500 nm
to 5 μm, and a deposition time of around 5 minutes.

The resulting carbon coated particles have a uniform coating of about 3 nm,
as shown on figure 24.

Example 11
Carbon coated LiFePO₄

10

Preparation of carbon coated particles

Carbon coated LiFePO₄ was prepared according to the method described in
example 1, using 600 mg of LiFePO₄ having a particle size ranging from 1 to 50
μm, and a deposition time of around 5 minutes.

15 The resulting carbon coated particles have a uniform coating of about 3 nm,
as shown on figure 25.

CLAIMS

1. A method for preparing particles having a core made of an electrode active material and a carbon coating, characterized in that said method comprises the steps of:

- 5 - providing active material particles;
- coating said particles with a carbon film by a physical vapor deposition (PVD) method using carbon as the carbon source;

wherein

- the particles remain are at a temperature lower than their decomposition
10 temperature; and
- the physical vapor deposition is a thermal vapor deposition method (TVD) comprising at least the following steps:
- i) an element made of carbon and surrounded by a metal filament, typically a tungsten filament, is present in a vacuum chamber;
- 15 ii) an active material in powder form is placed on a support in the vacuum chamber;
- iii) the powder is agitated by mechanical means;
- iv) the vacuum chamber is put under vacuum at a pressure lower than 10^{-1} Pa (10^{-3} mbar), more preferably lower than 10^{-2} Pa (10^{-3} mbar);
- 20 v) a current is applied to the tungsten filament to heat the carbon and generate carbon vapor in the chamber.

2. The method of claim 1, wherein the deposition rate is controlled by means of the current applied, a higher current applied providing a higher deposition rate.

25 3. The method of claim 1 or 2, wherein thickness of the deposit is controlled by the deposition time, a longer deposition time providing a thicker coating.

4. The method of claim 3, wherein the deposition rate is in the range of 0.05 to 0.4 nm/s.

30 5. The method of claim 3, wherein the deposition time in the range of 1 minute to 2 hours.

6. The method of claim 1, wherein the size of the active material particles to be coated is in the range of 5 nm to 700 μm .

7. The method of claim 1, wherein the element made of carbon is a carbon rod or a woven thread of carbon fiber.

8. The method of claim 1, characterized in that the electrode active material is a cathode active material selected from:

- 5 - transition metal oxides having spinel or layered type structures such as $\text{Li}_{1+x}\text{M}_{2-x}\text{O}_4$ with $0 \leq x \leq 0.3$ or $\text{A}_{1+x}\text{M}_{1-x}\text{O}_2$, with $0 \leq x \leq 0.3$; or
- oxides exhibiting a polyanionic framework with formula $\text{A}_y\text{M}(\text{XO}_4)_z\text{F}_t$ with $0 \leq y \leq 2$, $1 \leq z \leq 1.5$, $0 \leq t \leq 1$;
- lead sulphate;
- 10 - $\text{Ni}_{1-x}\text{M}'_x(\text{OH})_2$ where M' is transition metal; and

where M is selected from Mn, Fe, Co, Ni, Cu, V, Ti, Mg, Al, Zn or a mixture of them, X is selected from S, P, or Si and A is either Na or Li.

9. The method of claim 1, characterized in that the electrode active material is an anode material selected from silicon, tin, carbon, graphite, lithium
15 titanium oxide, lithium vanadium oxide, sodium titanium oxide, sodium vanadium oxide, titanium oxide, cobalt oxide, iron oxide, copper oxide, nickel oxide, iron fluoride, lead sulphate or an organic electrode material.

Fig. 1

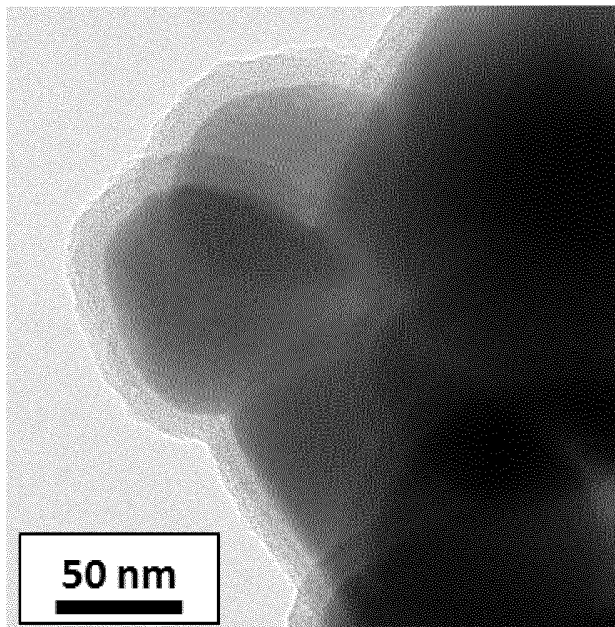


Fig. 2

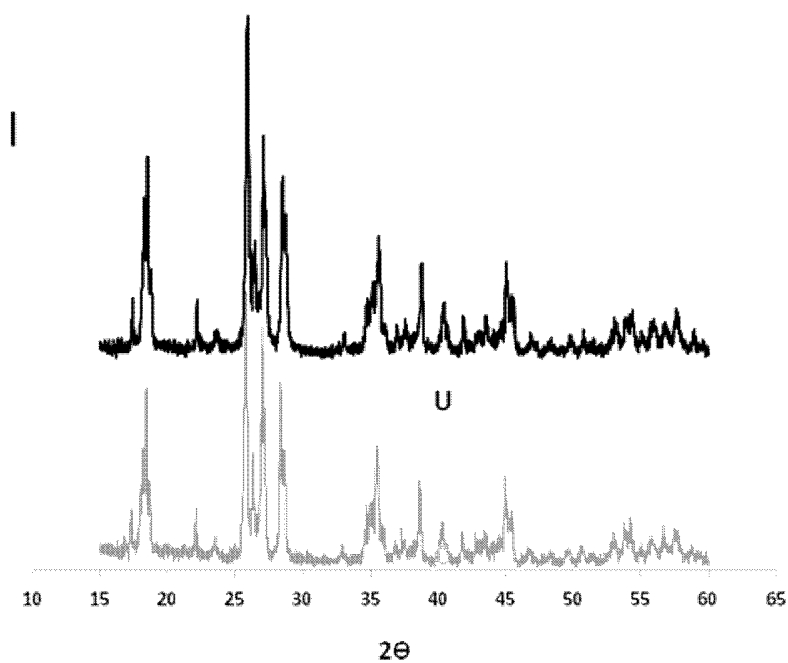


Fig. 3

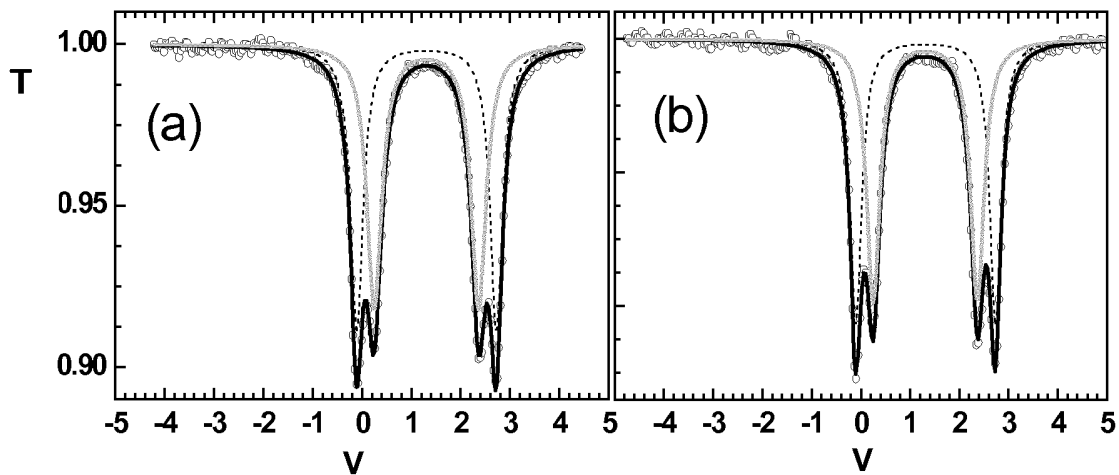


Fig. 4

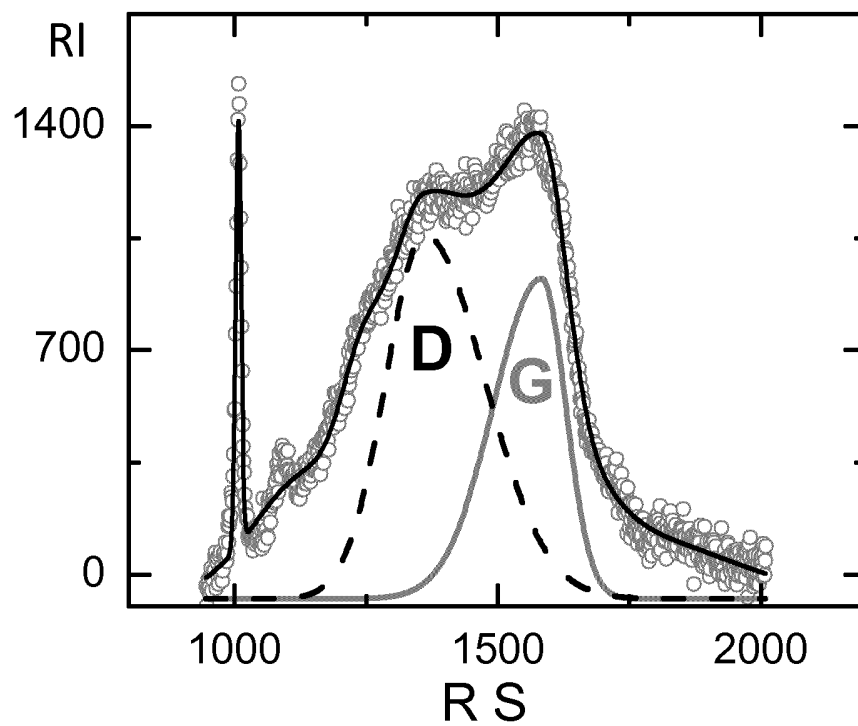


Fig. 5

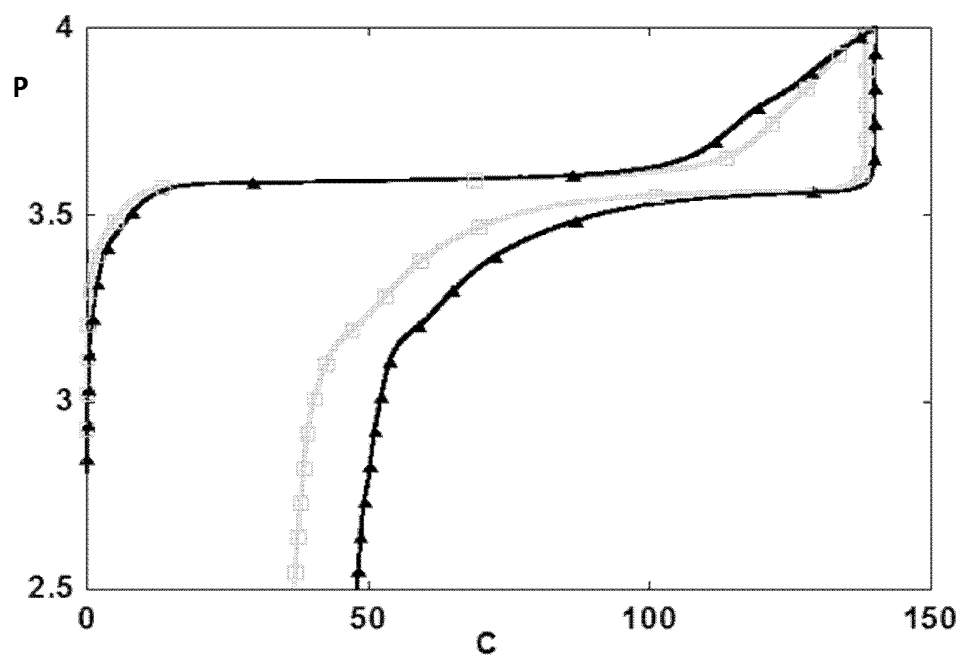


Fig. 6

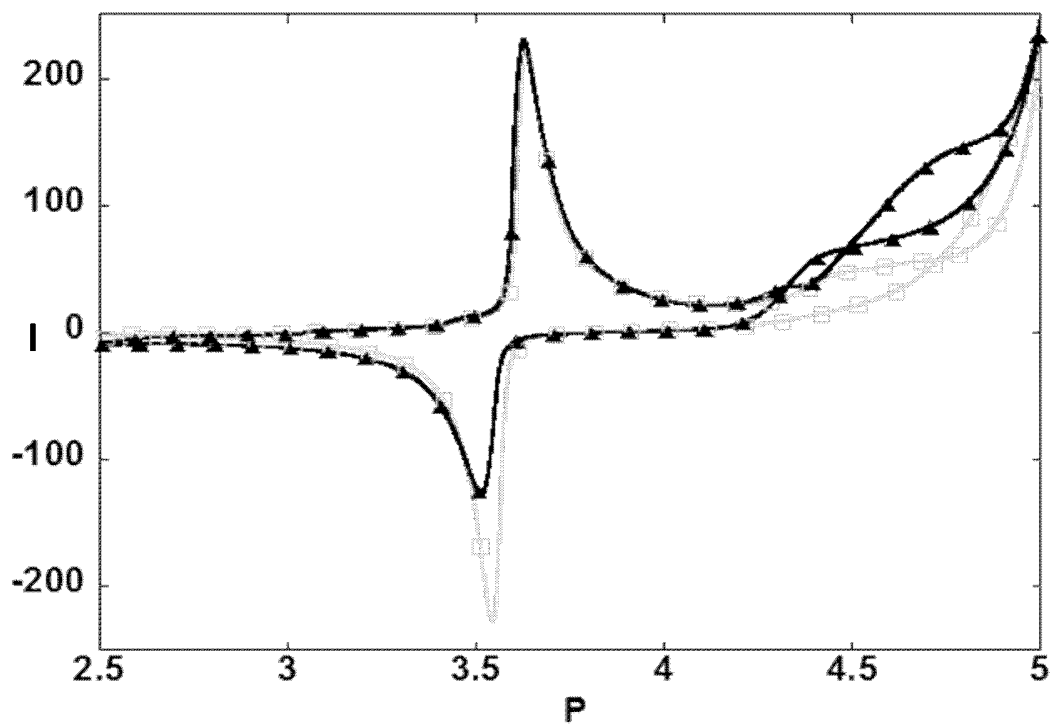


Fig. 7

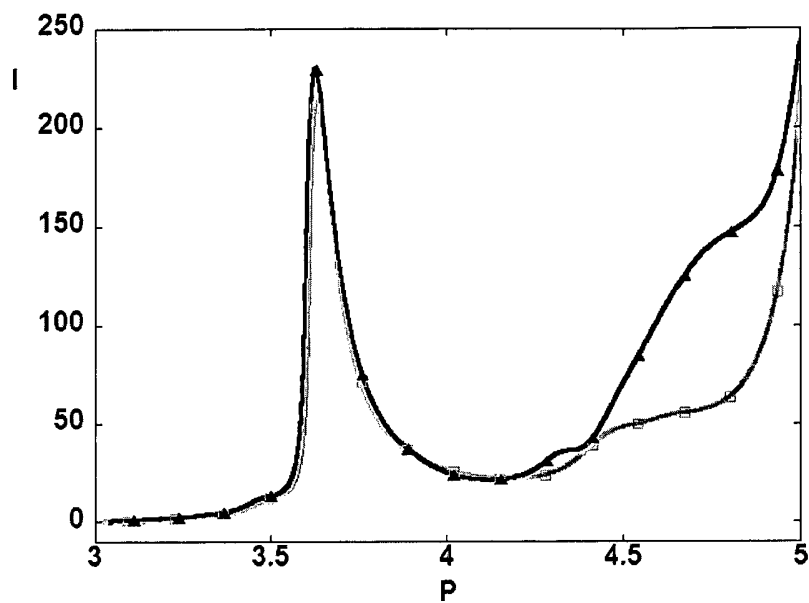


Fig. 8

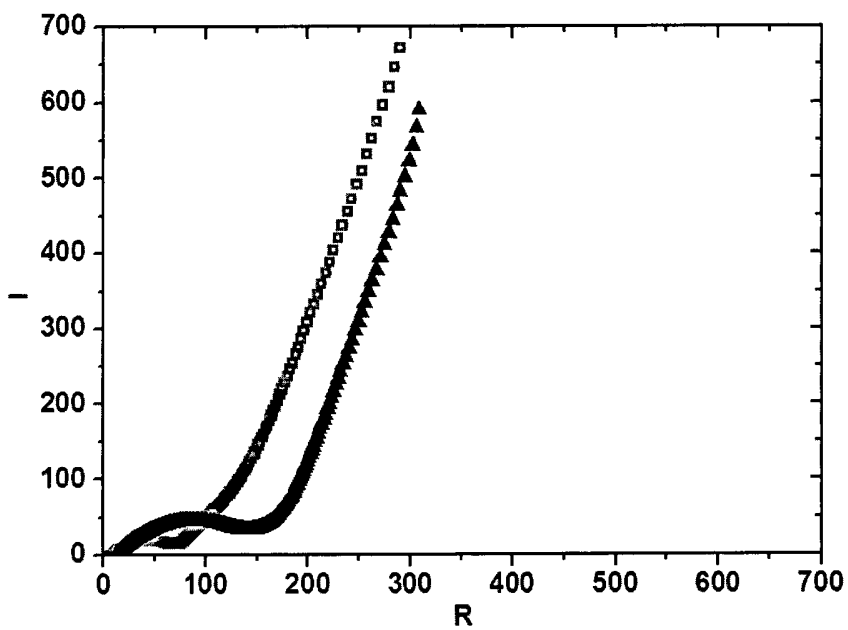


Fig. 9

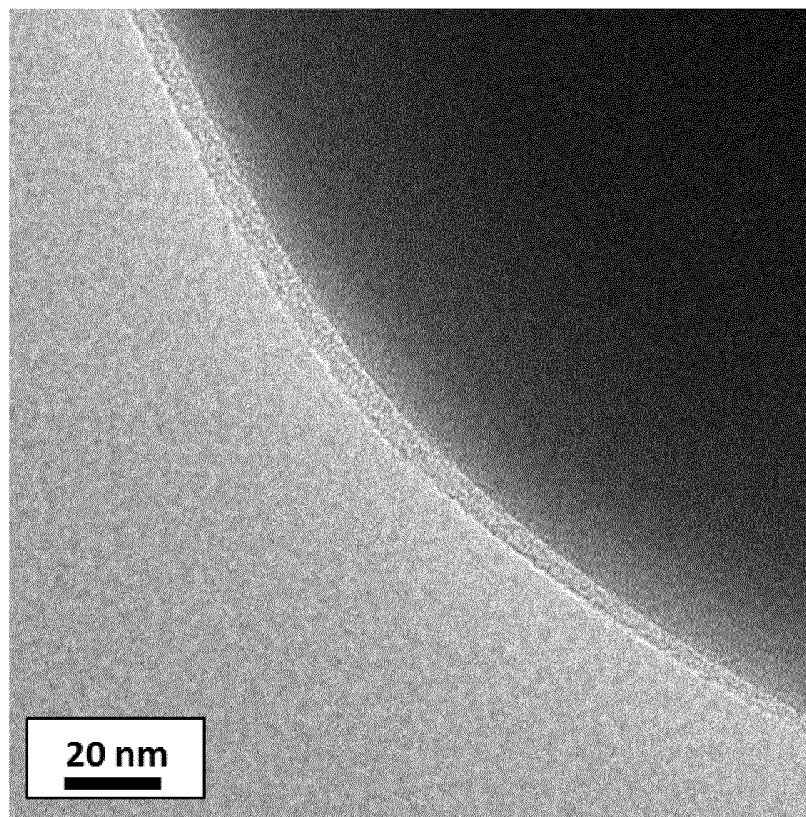


Fig. 10

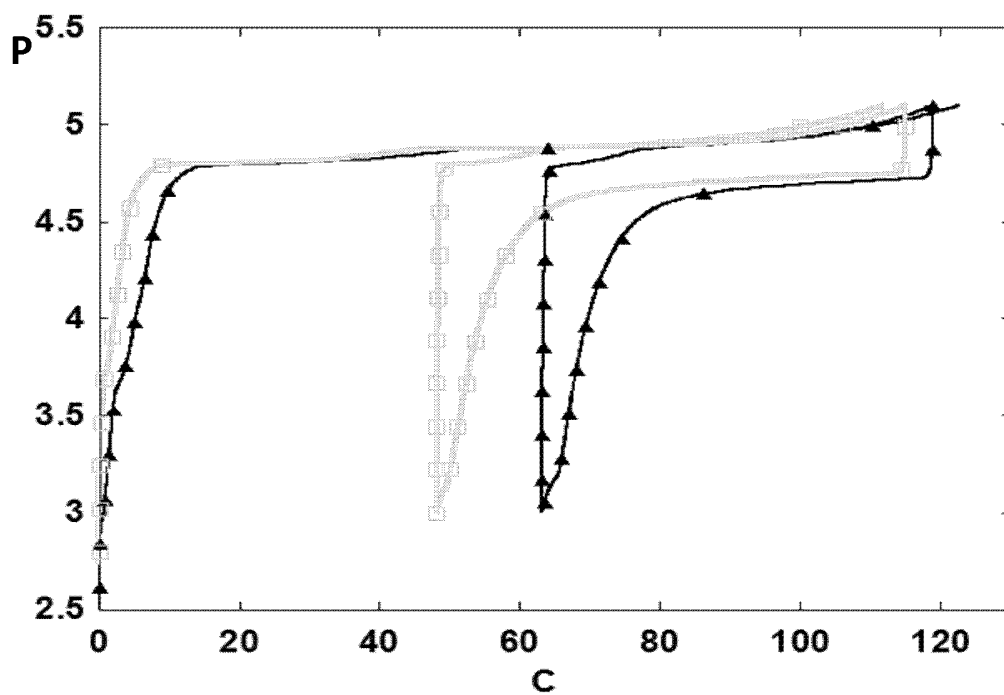


Fig. 11

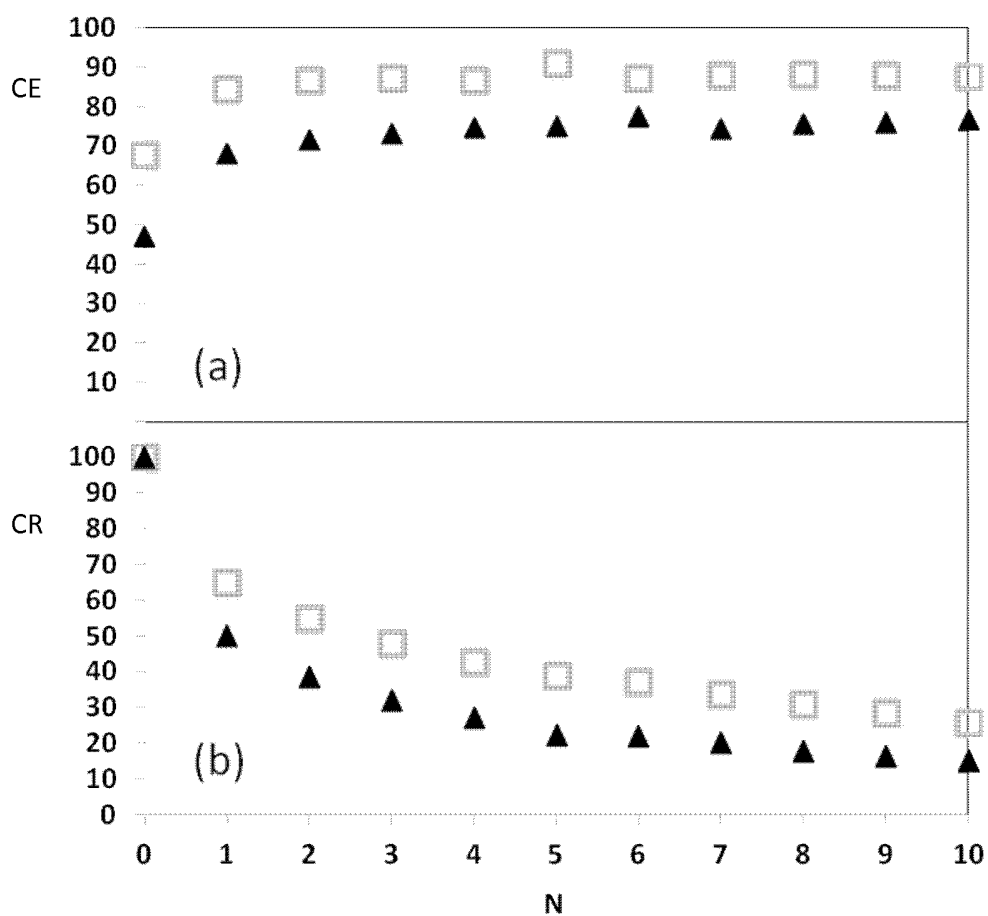


Fig. 12

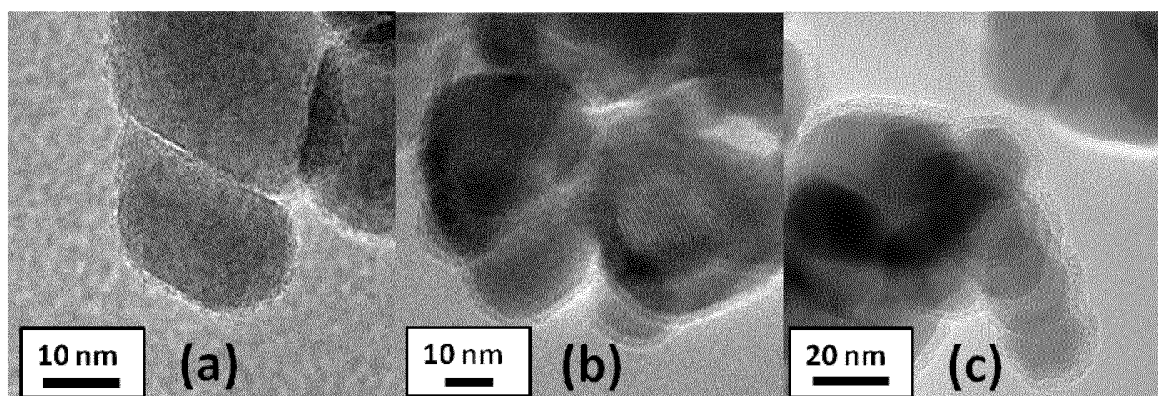


Fig. 13

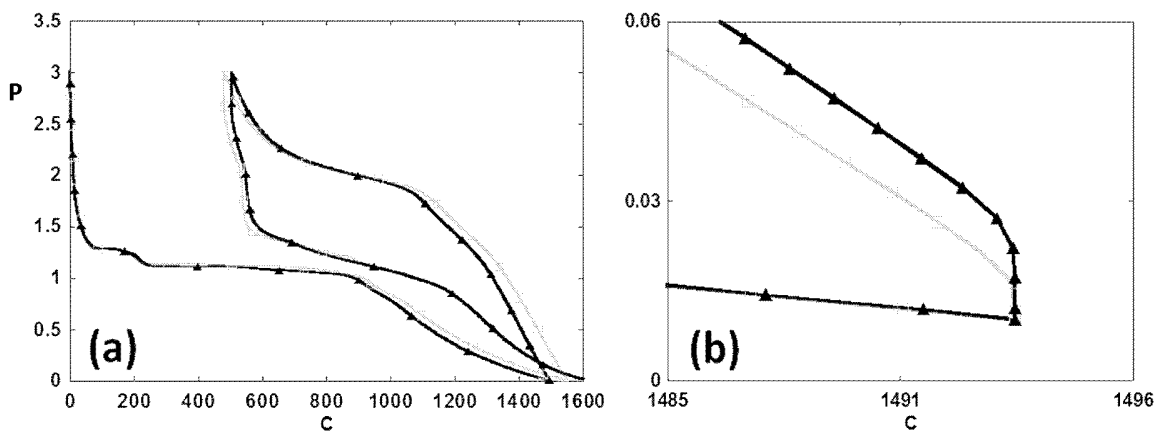


Fig. 14

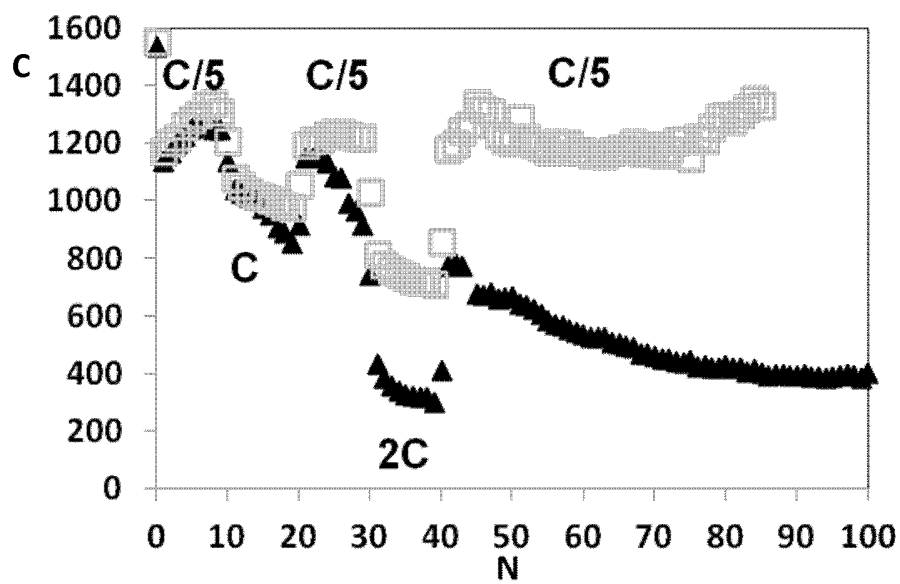


Fig. 15

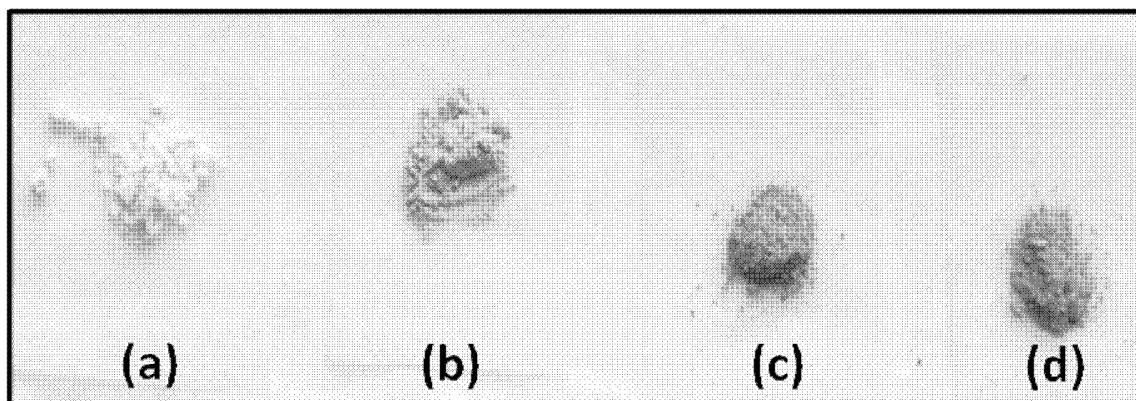


Fig. 16

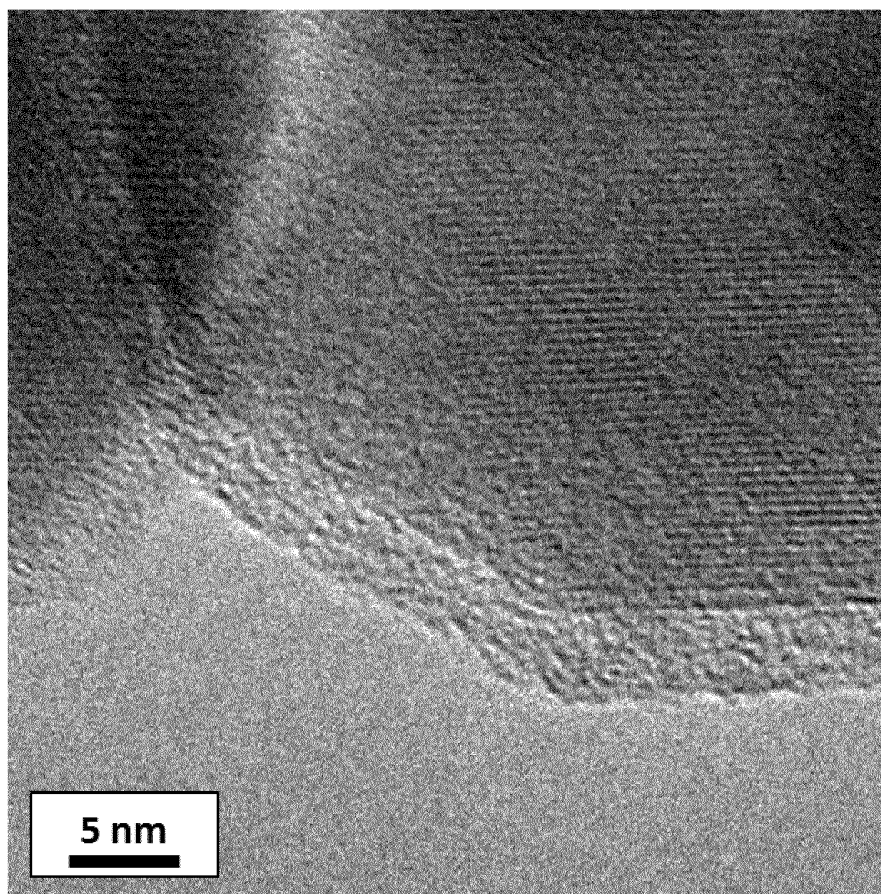


Fig. 17

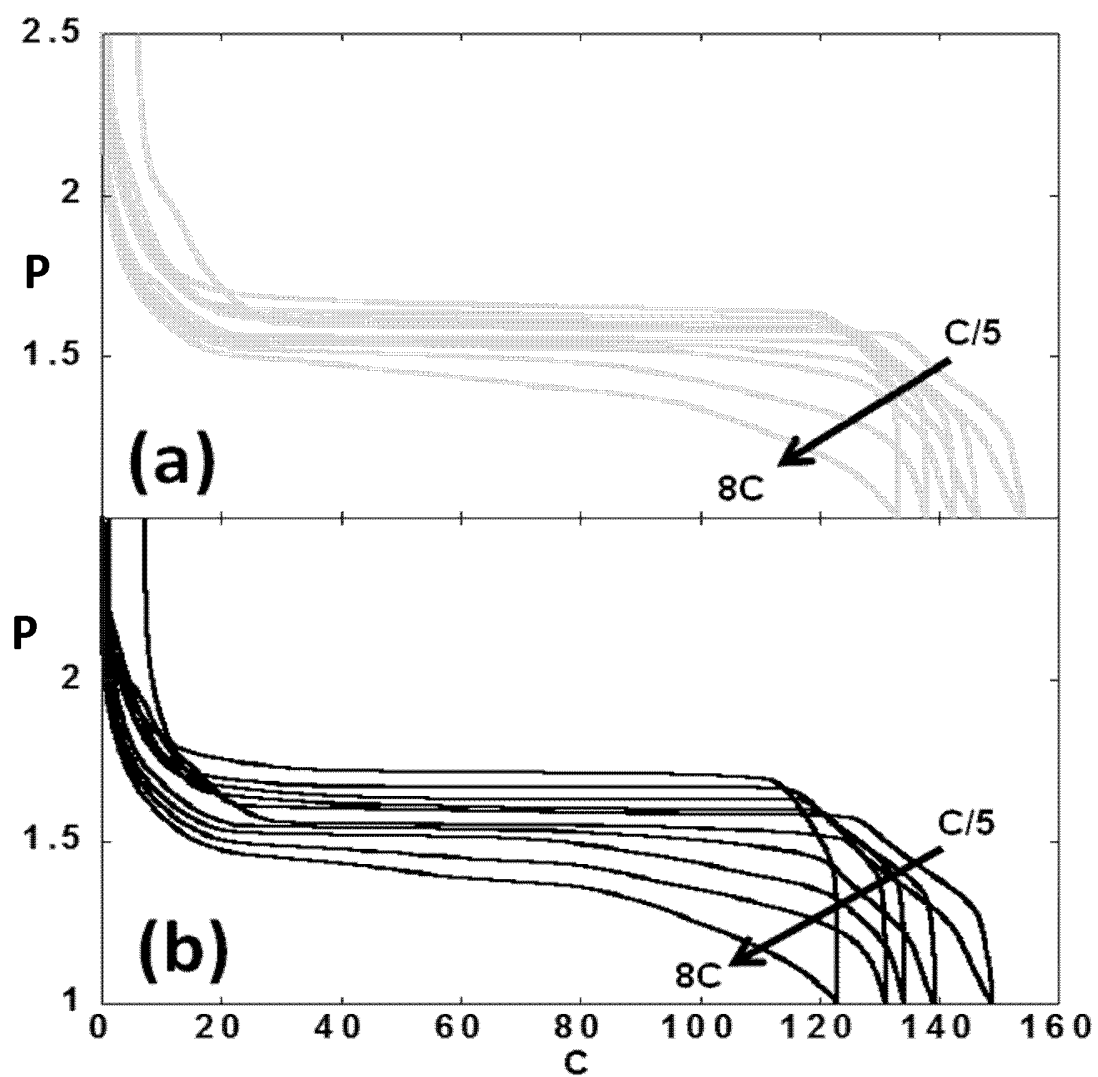


Fig. 18

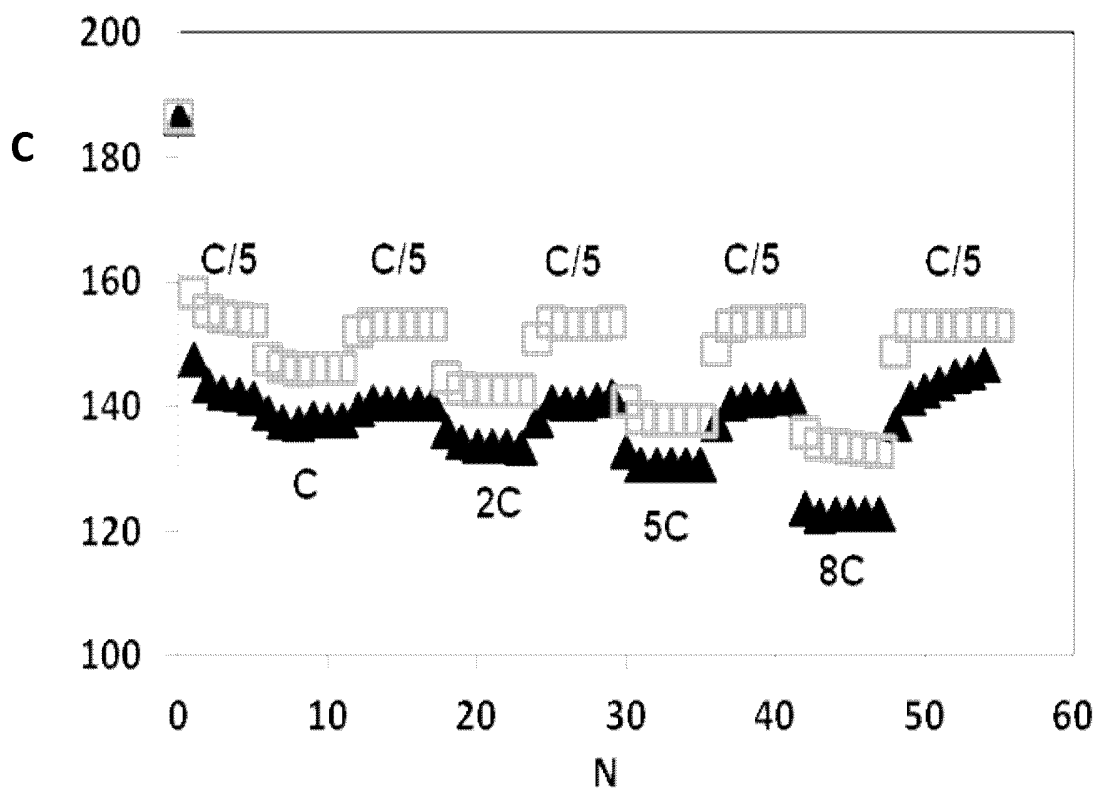


Fig. 19

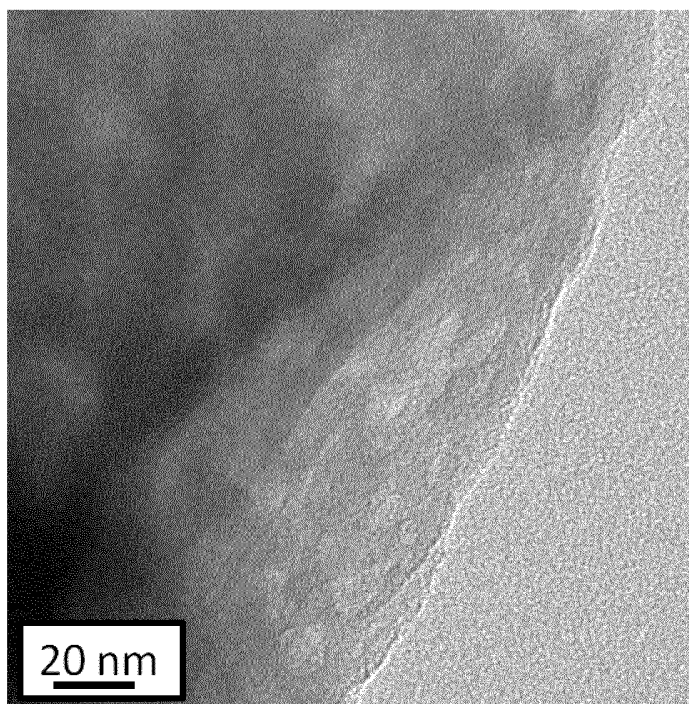


Fig. 20

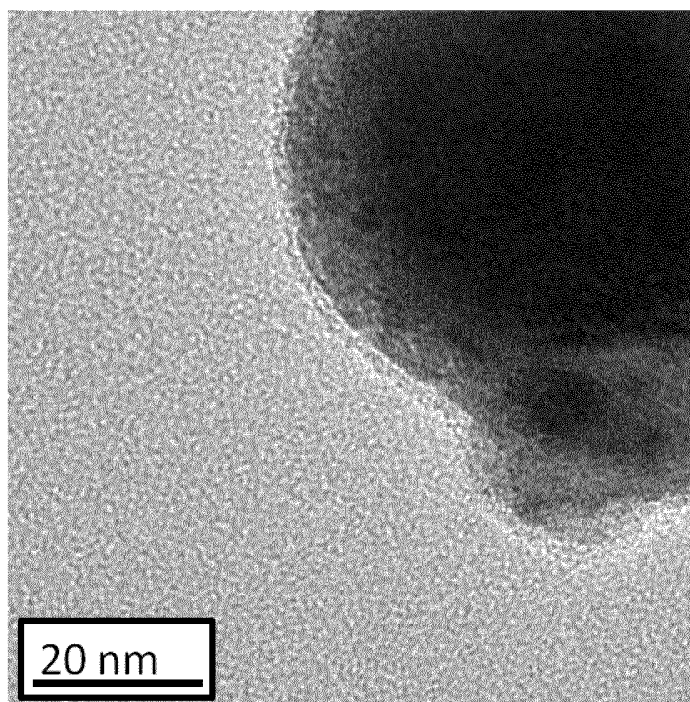


Fig. 21

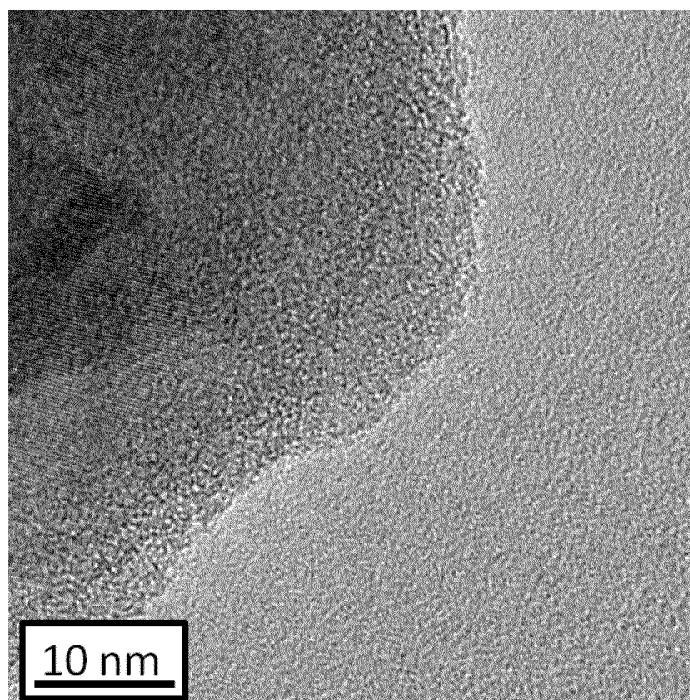


Fig. 22

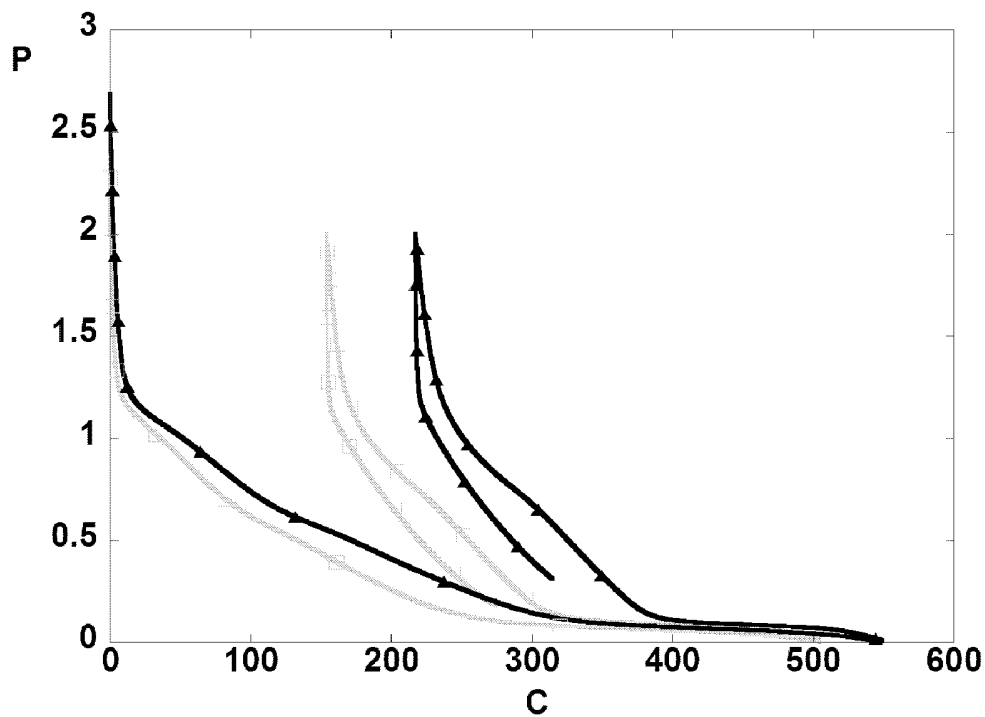


Fig. 23

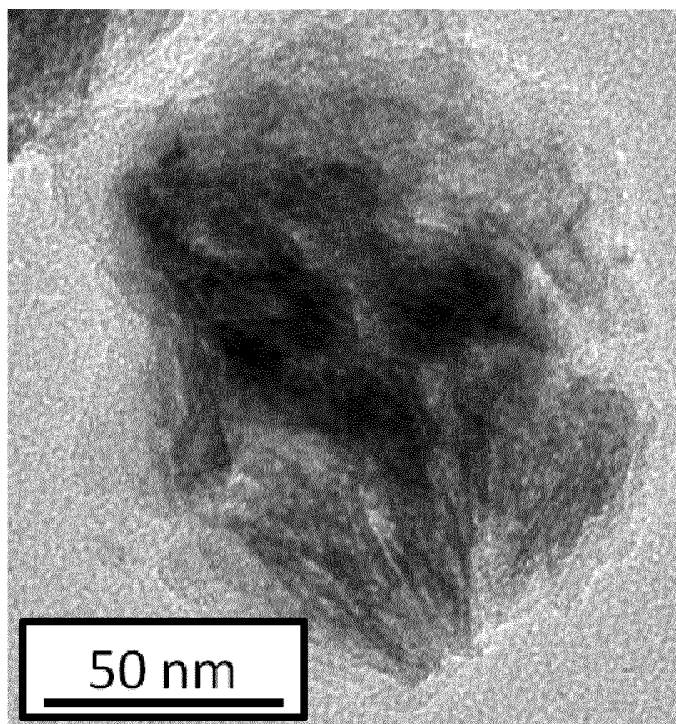


Fig. 24

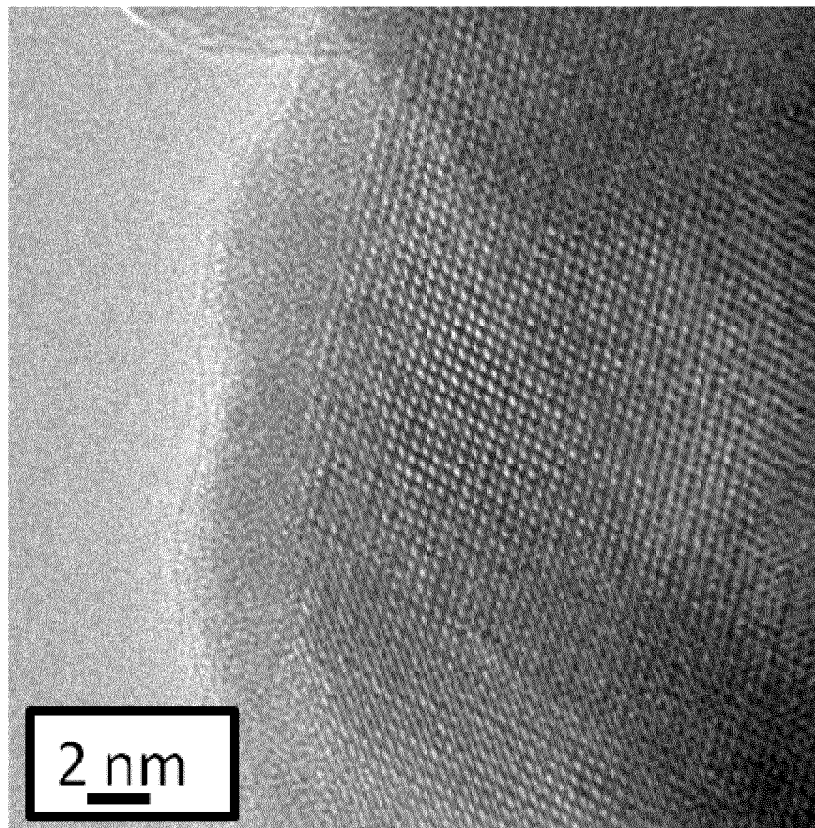
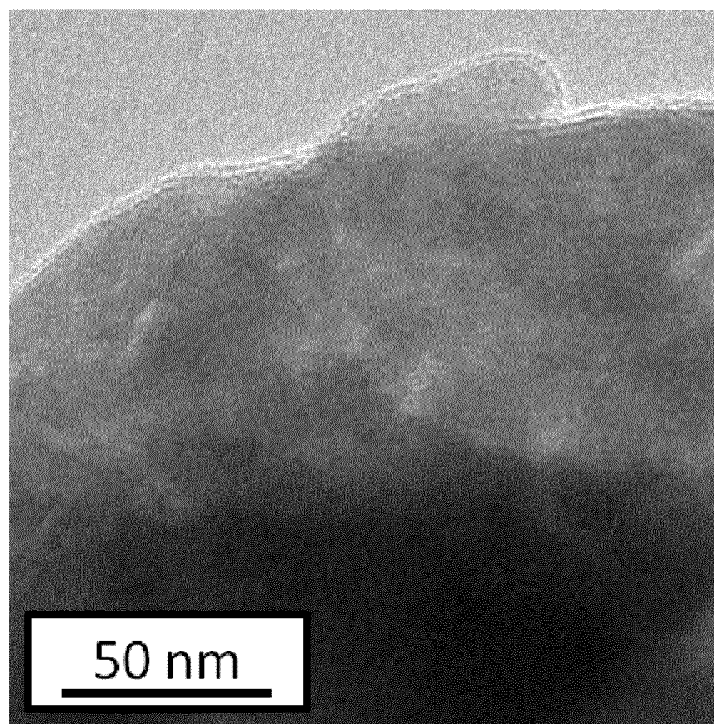


Fig. 25



INTERNATIONAL SEARCH REPORT

International application No PCT/EP2013/068107

A. CLASSIFICATION OF SUBJECT MATTER INV. H01M10/0525 H01M4/485 H01M4/505 H01M4/525 H01M4/587 H01M4/36 ADD. 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) H01M 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 practicable, search terms used) EPO-Internal, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
A	WO 2011/109457 A2 (UNIV TEXAS [US]; MANTHIRAM ARUMUGAM [US]; LIU JUN [US]; JAYAN BABY REE) 9 September 2011 (2011-09-09) paragraph [0094] - paragraph [0099]; figures 18-20 -----	1-9		
A	US 6 733 923 B2 (YUN KYUNG-SUK [KR] ET AL) 11 May 2004 (2004-05-11) cited in the application column 4, line 53 - column 7, line 2 -----	1-9		
A	EP 1 482 581 A2 (SONY CORP [JP]) 1 December 2004 (2004-12-01) paragraph [0057] - paragraph [0061]; table 1 ----- -/--	1-9		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents : <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search	Date of mailing of the international search report			
10 December 2013	17/12/2013			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Barenbrug-van Druten			

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/068107

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>HUIQIAO LI ET AL: "Enhancing the performances of Li-ion batteries by carbon-coating: present and future", CHEMICAL COMMUNICATIONS, vol. 48, no. 9, 1 January 2012 (2012-01-01), page 1201, XP055049890, ISSN: 1359-7345, DOI: 10.1039/c1cc14764a the whole document</p> <p>-----</p>	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/068107

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011109457 A2	09-09-2011	US 2013040201 A1 WO 2011109457 A2	14-02-2013 09-09-2011

US 6733923 B2	11-05-2004	JP 3624174 B2 JP 2003068281 A KR 20010084522 A US 2003039887 A1	02-03-2005 07-03-2003 06-09-2001 27-02-2003

EP 1482581 A2	01-12-2004	CN 1574421 A EP 1482581 A2 JP 3707617 B2 JP 2004349005 A KR 20040100906 A US 2004265698 A1	02-02-2005 01-12-2004 19-10-2005 09-12-2004 02-12-2004 30-12-2004
