



In situ high-resolution transmission electron microscopy synthesis observation of nanostructured carbon coated LiFePO₄

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ABSTRACT

In situ high-resolution transmission electron microscopy (HRTEM) studies of the structural transformations that occur during the synthesis of carbon-coated LiFePO₄ (C–LiFePO₄) and heat treatment to elevated temperatures were conducted in two different electron microscopes. Both microscopes have sample holders that are capable of heating up to 1500 °C, with one working under high vacuum and the other capable of operating with the sample surrounded by a low gaseous environment. The C–LiFePO₄ samples were prepared using three different compositions of precursor materials with Fe(0), Fe(II) or Fe(III), a Li-containing salt and a polyethylene-*block*-poly(ethylene glycol)-50% ethylene oxide or lactose. The *in situ* TEM studies suggest that low-cost Fe(0) and a low-cost carbon-containing compound such as lactose are very attractive precursors for mass production of C–LiFePO₄, and that 700 °C is the optimum synthesis temperature. At temperatures higher than 800 °C, LiFePO₄ has a tendency to decompose. The same *in situ* measurements have been made on particles without carbon coat. The results show that the homogeneous deposit of the carbon deposit at 700 °C is the result of the annealing that cures the disorder of the surface layer of bare LiFePO₄. Electrochemical tests supported the conclusion that the C–LiFePO₄ derived from Fe(0) is the most attractive for mass production.

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1. Introduction

LiFePO₄ is one of the competitive active cathode materials for Li-ion batteries. This material is attractive because of its low cost, non-toxicity, and remarkable thermal stability [1]. The electronic conductivity, however, is low. To overcome this problem, the LiFePO₄ particles must be coated with a thin carbon layer for use in Li-ion batteries [2]. This has been recognized since years for large particles. However, the decrease in size of the particles has been sometimes considered as an alternative to increase the electronic conductivity. In an extreme case, it has even been predicted that carbon coating was not needed if the size of the particles was reduced to few tens of nanometers [3]. This, however, is a misunderstanding of the role played by the carbon deposit. Indeed, the reduction in size implies that the path of an electron in any given particle to reach the surface is smaller on average. However, the main problem of the conductivity for the electron is not to reach the surface; it is to be drained to the collector. The first role of the carbon layer is thus to create a electric contact between the par-

ticles, so that an electron, once it has arrived at the surface of the particle from which it has been extracted, can move to the collector by following the connected network of the conductive carbon of the composite up to the collector. Actually, the reduction in size of the particles results in an increase of their concentration, and makes the electric contact between them even more important. In addition, non-coated LiFePO₄ particles have a disordered surface layer [4], which will result in an increase of the electric resistance. The second role of the carbon coating is to cure the structural disorder at the surface, thus reducing the electric resistance in the surface layer, although we do not know yet whether this effect is due to an interaction with the carbon, or is due to the re-crystallization of the surface layer upon heating the sample during the carbon coating process. Since the ratio surface layer over volume is increasing, so does the importance of this carbon effect when the size of the particles is reduced. Therefore, the coating of the particles is mandatory for particles of any size, and is even more important with small particles than with bigger ones. These aspects and another important role of the carbon deposit to avoid local heating due to the Branly effect are discussed in more details in a recent review paper [5]. The important role played by the surface and the carbon coat to obtain the C/LiFePO₄ composite with optimized electrochemical properties were the motivation for the present

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investigation of their structural properties, by in situ electron microscopy.

The synthesis and characterization of LiFePO_4 and other promising cathode materials has received extensive attention. However, conventional techniques involving heat treatment in high-temperature furnaces, followed by materials characterization, can be extremely long processes that can easily miss the best set of conditions for the synthesis of new compounds. Consequently, there is a strong incentive to use in situ techniques to directly observe changes in chemical composition and structure that occur in real time during synthesis or chemical processes. By directly observing the structural changes in materials and/or the synthesis of new compounds under different temperatures and even different atmospheres, the efficiency of the synthesis processes can be dramatically improved.

As mentioned above, to enhance the conductivity of metal oxides used as cathode materials, carbon is commonly added as a conductive matrix or as a coating. When the metal oxide particles are coated with a thin layer of carbon (~ 1 wt%) a few nanometers thick, it is very difficult to readily ascertain that the carbon is having the desired effect unless a technique is available to probe the properties of the carbon. High-resolution transmission electron microscopy (HRTEM) is one technique to examine the properties and the structure of the carbon layer. In particular, in situ transmission electron microscopy is uniquely well suited to study atomic-level transformations in the microstructure of electrode materials, following events in real time the morphological as well as the crystallographic changes that occur during heat treatment because of its high image resolution in observing crystal lattices. However, there are some experimental limitations that must be solved, such as sample preparation (i.e., suitable thickness, electron transparency), sample environment (i.e., vacuum, low partial pressure of inert gas), sample manipulation and temperature control. Consequently, *ex situ* TEM analysis is a more common approach to study changes in electrode materials [6–11] that typically involves TEM examination of a sample before and/or after an experimental procedure. To the best of our knowledge, there are very few in situ TEM studies of cathode materials for Li-ion batteries. However, Chung et al. [12] conducted in situ TEM studies on the synthesis of LiFePO_4 that is relevant to Li-ion battery technology. Collecting a series of TEM images during the crystallization of amorphous LiFePO_4 at 450°C , they observed the presence of metastable transient phases at an atomic scale during the crystallization of an olivine-type metal phosphate, which suggested a new description for the kinetic pathway of crystallization in complex inorganic systems.

In this paper, we present results of HRTEM studies of the structural transformations that occur during the synthesis of carbon-coated LiFePO_4 (C- LiFePO_4) and heat treatment up to 900°C . As a result, we find that the synthesis of LiFePO_4 starts at circa 400°C , but the carbon coat is deposited at higher temperature. The carbon coat is not uniform at 600°C and is stabilized under the form of a uniform 3 nm thick layer only after 45 min spent at 700°C .

To distinguish between the effect of the carbon and the effect of the annealing process, we have made similar experiments on LiFePO_4 particles that have been prepared by hydrothermal process and are not carbon-coated. In that case, the surface of LiFePO_4 is disordered in a surface layer about 10 nm thick. At 700°C , however, the full crystallisation of the surface layer is achieved after 16 min.

2. Experimental

2.1. Synthesis

A variety of preparation techniques have been employed in our laboratory to synthesize LiFePO_4 [13–16]. Therefore, only a

brief summary of the procedures is described here. In this study, C- LiFePO_4 samples were prepared using different compositions of precursor materials: (i) stoichiometric amount of Li_2CO_3 (Limtech, 99.9%) and FePO_4 powders (Budenheim, grade E53-81), were mixed together with approximately 5% by weight of a polymeric carbon additive, polyethylene-*block*-poly(ethylene glycol)-50% ethylene oxide (Aldrich), which is designated as method A; (ii) Fe, LiOH (Aldrich), H_3PO_4 (Aldrich) and lactose (Aldrich) were dissolved in water, then the spray was dried to remove the water (method B); (iii) a mixture of FeSO_4 (Aldrich), LiOH and H_3PO_4 (Aldrich) was heated at 220°C for 3 h, then lactose was added, dissolved in water and finally the product was annealed at 700°C for 5 h (method C). Finally some C- LiFePO_4 powders were prepared in a laboratory Teflon-lined autoclave by a hydrothermal process [17].

For comparison, pristine LiFePO_4 specimens (non coated with carbon) were prepared in a laboratory Teflon-lined autoclave by the hydrothermal route. The stoichiometric amount of the precursors, jet-milled iron oxalate, H_3PO_4 and LiOH were thoroughly mixed together. The autoclave was filled with distilled water and maintained at 165°C for 4 h, and then cooled down to room temperature.

2.2. In situ studies

The in situ studies were conducted in two different transmission electron microscopes manufactured by Hitachi High Technologies: (i) a H-9500 300 kV LaB_6 TEM and (ii) a HD-2700C dedicated STEM. For the present studies, the H-9500 was operated with a partial pressure of about 12 mPa of nitrogen, while the studies in the HD-2700C were done under high vacuum. The HD-2700C STEM provides very high-resolution images and superior elemental analysis capabilities than a normal TEM. However, heat treatment at elevated temperatures under a nitrogen atmosphere provides more representative conditions of synthesis processes, and for that reason, synthesis experiments were conducted in the H-9500.

The H-9500 environmental TEM utilizes a LaB_6 electron source and can be operated at an accelerating voltage of 300 kV or lower. This TEM is capable of a magnification range from $200\times$ to $1.5 \times 10^6\times$, and has resolution of 0.10 nm (lattice) and 0.18 nm (point-to-point). It has special vacuum configurations for in situ environmental TEM, and for the present study it was operated at 300 kV.

The HD-2700C employs a cold field emission electron source operated here at an accelerating voltage of 200 kV. It has a spherical aberration corrector developed in collaboration with CEOS GmbH. This STEM is also equipped with an EELS Spectrometer (specially designed Enfina from Gatan) and a new silicon drift detector (SDD) for energy dispersive X-ray spectroscopy (EDS) that was specifically designed by Bruker. This microscope is installed in an isolated building, inside a commercially available cold storage room with magnetic shielding and equipped with a temperature control system that limits the temperature fluctuations to about 0.15°C in a 24-h period. By correcting the spherical aberration, a resolution of less than 0.10 nm can be achieved in dark-field STEM mode. In fact, a resolution of 0.078 nm was achieved in high-angle annular dark-field (HAADF) in direct observation on a (1 1 2) Si sample.

The thermal studies of the samples in the HD-2700C was conducted with a protochips heating holder using a fast heating semiconductor support device and a Hitachi sample-heating holder equipped with a coiled tungsten heating wire that is capable of temperature up to 1500°C , while still providing atomic-resolution images. Fig. 1a shows a photograph of the heating insert with the coiled tungsten heater element that is used in the holder, which is inserted in the STEM. The powders are simply dispersed on the coiled tungsten wire, as illustrated schematically in Fig. 1b. A low-resolution STEM micrograph of the sample particles that are dispersed on the tungsten wire is presented in Fig. 1c. For the

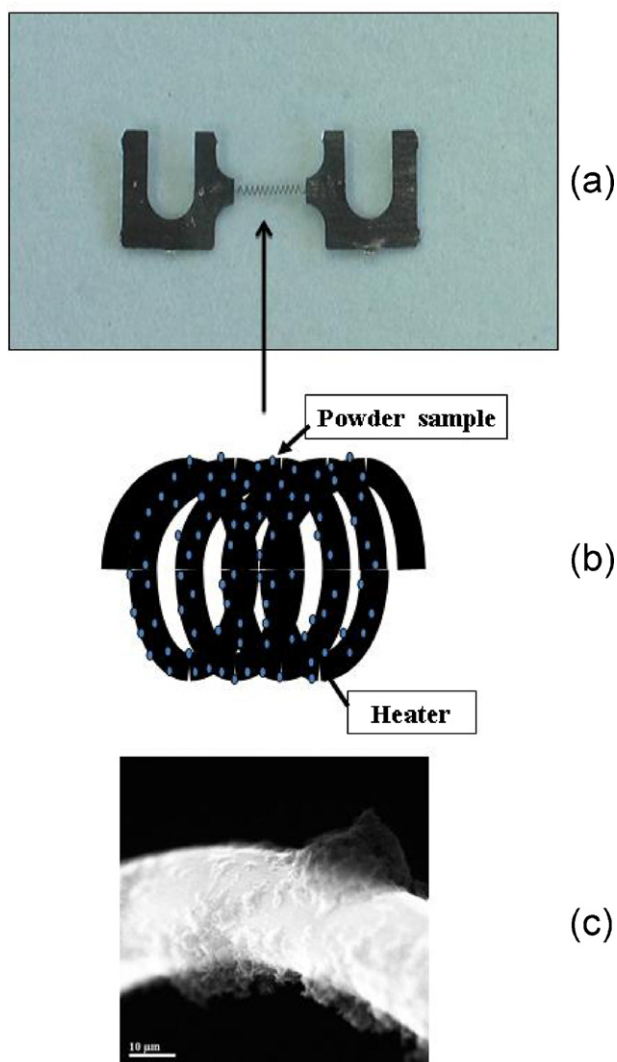


Fig. 1. (a) Photograph of insert with coiled tungsten heater element used in sample heater, (b) schematic representation of heater coil with attached powder sample (courtesy Hitachi High Technologies) and (c) low-resolution STEM micrograph of sample particles on the heating coil (10-micron marker).

presents experiments the error on the temperature (based on the readout of the current in the W wire) was estimated at about 50 °C.

A similar type of heating element was used in the H-9500. However, the sample holder in this microscope has a small inlet tube that allows gases to be injected near the sample. The H-9500 microscope has a built-in differential pumping system for conducting environmental TEM studies [18]. This arrangement allows the sample to be directly exposed to the electron beam and to the gas environment in the sample chamber. Fig. 2 represents a typical heating experiment with the corresponding time at which the sample reached a particular temperature. During this period of time, structural observations were done on the powders. The N₂ pressure in the TEM remained constant at 12 mPa during heating to 700 °C. We have shown earlier that the N₂ atmosphere is reducing because of the presence of hydrogen impurity in it [19]. However, this reducing power was due to an immersion in N₂ at atmospheric pressure, and it was actually needed to avoid the formation of Fe³⁺ impurities in the synthesis at very high temperature of LiFePO₄ in the molten state, since such impurities were found in case N₂ was replaced by argon [19]. Due to the dilution at a pressure as low as 12 mPa in the present work, however, the nitrogen will not play such a role. Nevertheless, the presence of hydrogen during the

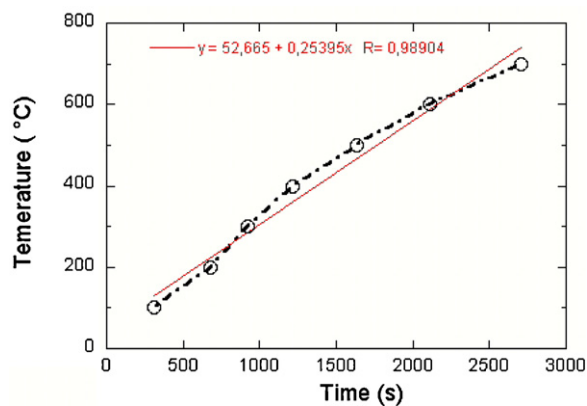


Fig. 2. A typical in situ heating experiment with the corresponding time at which the sample reached a particular temperature.

synthesis is mandatory, because we have shown [20] that the crystallization of LiFePO₄ at the temperatures explored in the present work is simply impossible following the synthesis route described in Section 2.1, whether carbon black is added or not to the precursors. The reason is that any reducing power of carbon (carbothermal effect) simply does not exist at such low temperature (i.e., below 1000 °C) [20]. The reducing hydrogen agent here, whether it is under the form a hydrogen gas or any gaseous hydrocarbon, comes from the polymer, or the lactose, or the glucose, depending on the synthesis process A, B or C. Indeed, the investigation of the decomposition of these organic compounds shows that the hydrogen that they contain is liberated at low temperature, allowing the start of the synthesis of LiFePO₄ at 400 °C [20], which has been confirmed independently in [12].

2.3. Electrochemical measurements

Electrodes containing C–LiFePO₄ that were prepared using precursors in methods A, B and C were evaluated in electrochemical cells. A Li counter electrode was used and the electrolyte consisted of LiPF₆ + EC + DEC from Ube (Japan). The electrochemical measurements were obtained at C/24 rate, while electrochemical tests of electrode without coating and with carbon-coating were carried out at C/12.

3. Results and discussion

Fig. 3 presents the bright field (BF) images obtained during heating under vacuum of a precursor mixture described as method A from room temperature to 700 °C, with BF-STEM images obtained at room temperature, 500, 600 and 700 °C. The arrow in the figure is used as a point of reference for the needle-like structure of Fe particles. The reaction mechanism is very complex during heating from room temperature to 500 °C. This is the temperature range where the organic additive decomposes and the reducing hydrogen agent is liberated, allowing LiFePO₄ to be formed. On another hand, one cannot detect any major structural changes between 500 and 600 °C. At 600 °C, however, changes can be seen, as the carbon layer is being formed. At 700 °C, the image of the Fe structure is no longer evident, and the BF-TEM images reveal the formation of large carbon coated well crystallized particles.

Figs. 4 and 5 display a sequence of BF-TEM images and electron diffraction micrographs, respectively, during different stages of heat treatment from 200 to 700 °C of the same precursors but this time under 12 mPa of nitrogen. Again, these results show no evidence for the formation of LiFePO₄ at temperatures less than 300 °C, in agreement with the X-ray analysis previously reported

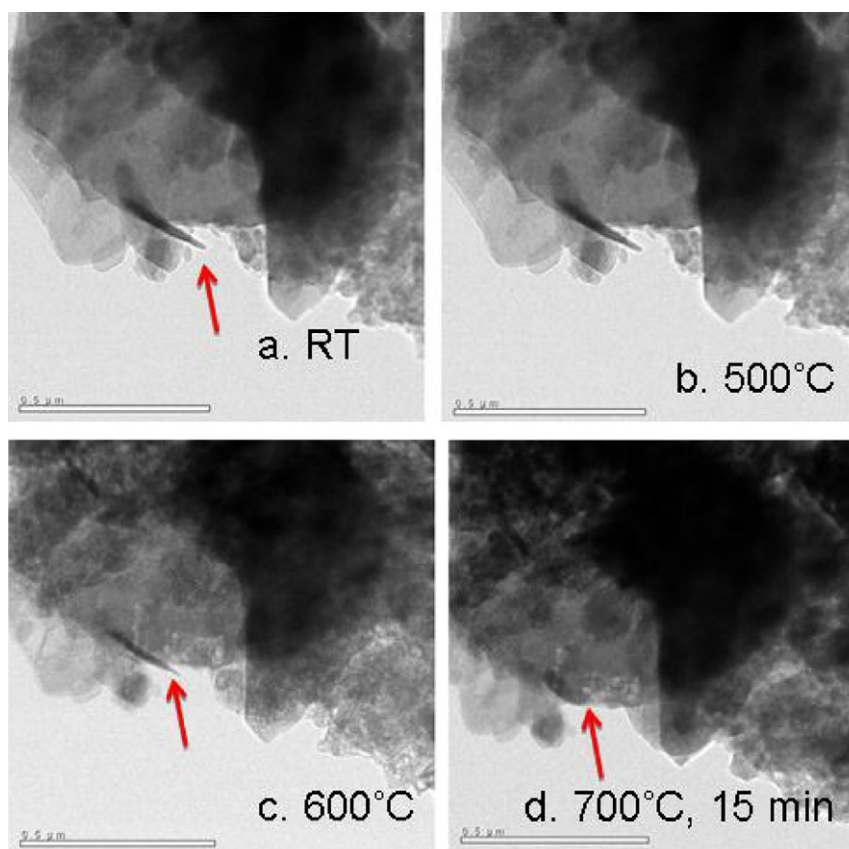


Fig. 3. (a) BF-STEM image of a mixture of FePO_4 , Li_2CO_3 and a polymer under vacuum at (a) room temperature (b) 500, (c) 600 and (d) 700 °C.

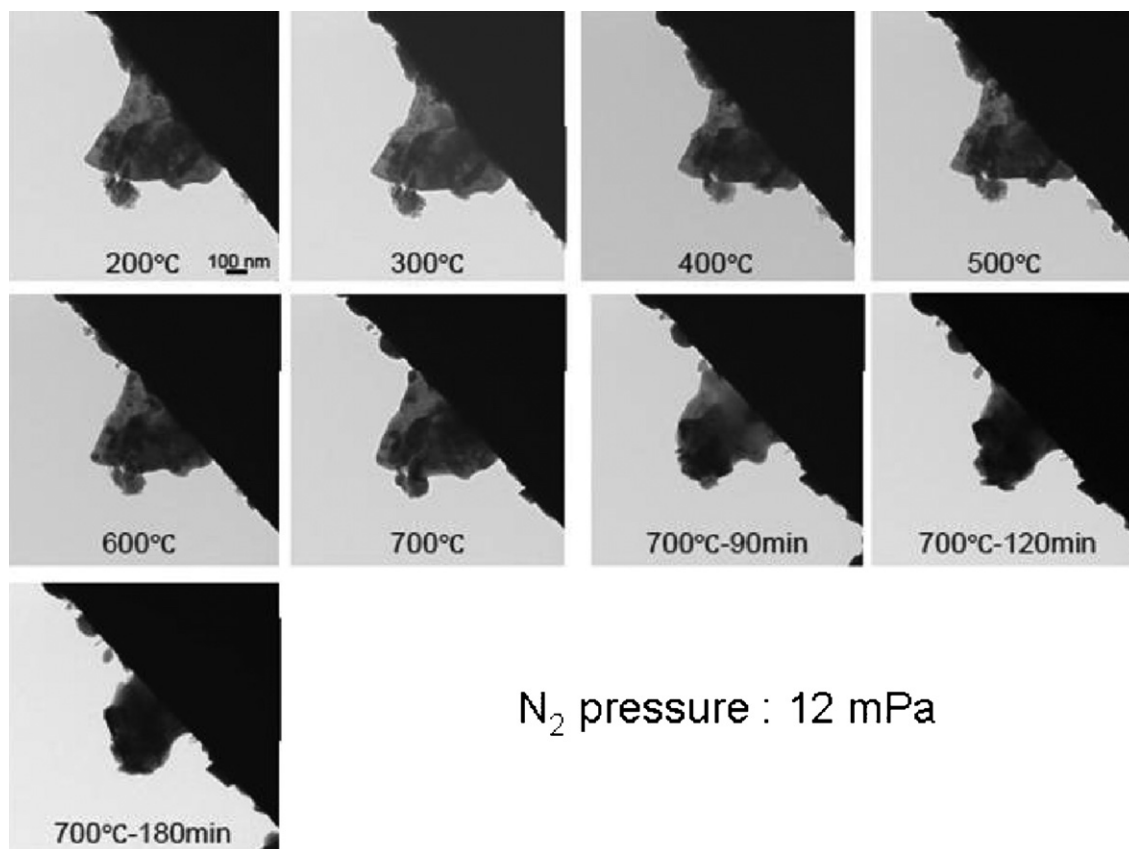


Fig. 4. Sequence of TEM micrographs obtained during heat treatment of a mixture of FePO_4 , Li_2CO_3 and polymer (method A) under 12 mPa of nitrogen to 700 °C.

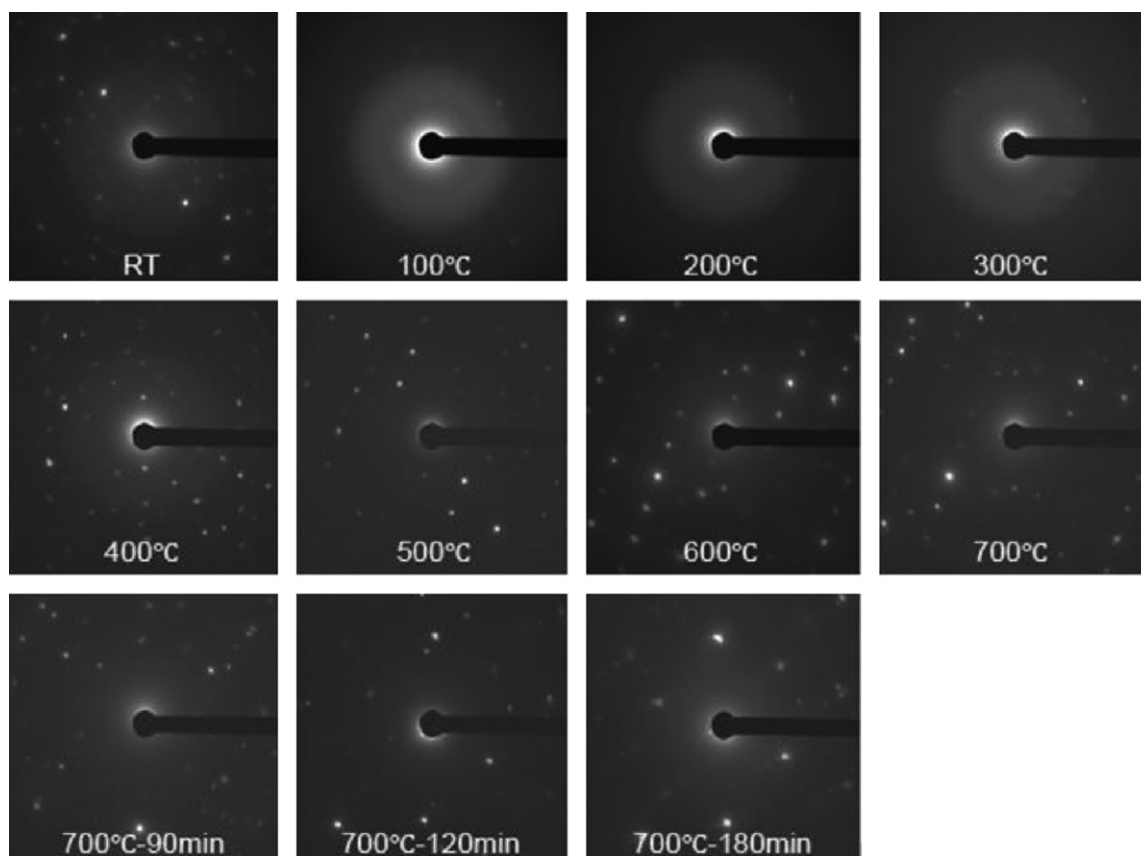


Fig. 5. Electron diffraction studies of the materials presented in Fig. 3 (method A) obtained during heat treatment from room temperature to 700 °C under 12 mPa of nitrogen.

[20]. At 400 °C, the formation of LiFePO_4 begins, but the BF-TEM images show very little structure change up to 700 °C. At 700 °C, the TEM images, with extended heating to 180 min, show changes in the morphology as a function of time (see video 1). Further details are evident in the selected area electron diffraction (SAED) patterns in Fig. 5, which shows quite complex changes in the structure of the powder as a function of the heating temperature. The XRD diagram at room temperature is composed of the diffraction patterns from the basic components. As soon as the powder is heated to temperature above 100 °C, we see its structural transformation mainly to an amorphous phase, with only small crystalline diffraction dots. The exact nature of this amorphous phase remains unclear. However, the formation of an amorphous LiFePO_4 has been observed earlier from the drying process of co-precipitated precursor materials [21]. Above 300 °C we observe the appearance of more diffraction dots and the material has clearly crystallized around 400 °C as expected [20]. From 400 to 700 °C we continue to observe structural changes associated to the growing of LiFePO_4 crystallites, as observed in the high-resolution images of Fig. 5. More detailed studies are presently on-going to better understand these structural transformations.

Fig. 6 shows a sequence of captured HR-TEM video images of the sample observed by BF-TEM in Fig. 4. In particular, the observations were directed at following the changes to the carbon surface layer as a function of time at 700 °C (video 2) from the moment, where the temperature has been reached after heating at the rate of $0.25\text{ }^\circ\text{C s}^{-1}$, fast enough so that the carbon did not have time to coat the particles. The first image (upper left) shows that the carbon layer is not well developed yet, but instead exhibits some disorganized structure. However, this layer progressively changes, and after 45 min at 700 °C (bottom right), a well-defined and homogeneous carbon layer is formed with a thickness of about 3 nm, as can be seen in better details in Fig. 7a. In addition, one remarkable

result is that the interface between the carbon and the LiFePO_4 particle at the end is abrupt. The well-crystallized structure of LiFePO_4 is evidenced by the atomic *ab* planes observed on the TEM images (see also Ref. [16]); these atomic planes end up to the carbon layer in Fig. 7a. This result confirms the assumption [19] that the carbon coating is efficient to cure the well-known disorder of the surface layer of uncoated LiFePO_4 . When the sample is cooled back down to 25 °C, neither the carbon layer nor the interface with LiFePO_4 has shown any change.

Moreover, if we increase the temperature to around 750 °C, we can observe in Fig. 7b some decrease in the homogeneity of the carbon layer. The properties of the carbon layer are key parameters for the success of olivine as the positive electrode to approach its theoretical capacity 170 mAh g^{-1} . These observations have some practical implications for mass production of C- LiFePO_4 . The optimum temperature for synthesis seems clearly to be 700 °C, as mentioned earlier. In addition, according to our studies (see video 2), the heating time at this temperature needed to form a stable carbon layer can be smaller than 45 min. By decreasing the heating time at 700 °C, the processing time and energy cost to heat the synthesis furnace can be reduced.

In another study we look at the same kind of in situ processing, but this time using precursor mixture described as method B. Fig. 8 presents a sequence of BF-TEM micrographs as well as electron diffraction patterns taken at different stages of heat treatment from RT to a temperature near 650 °C under 12 mPa of nitrogen. Again, these results show no evidence of major morphological changes below 650 °C. The electron diffraction images indicate that below this temperature the powder is composed of some crystalline and amorphous materials. At 650 °C, we can observe a transformation to a more crystalline structure. The high magnification micrograph taken at 650 °C shows a very nice crystalline structure of LiFePO_4 ,

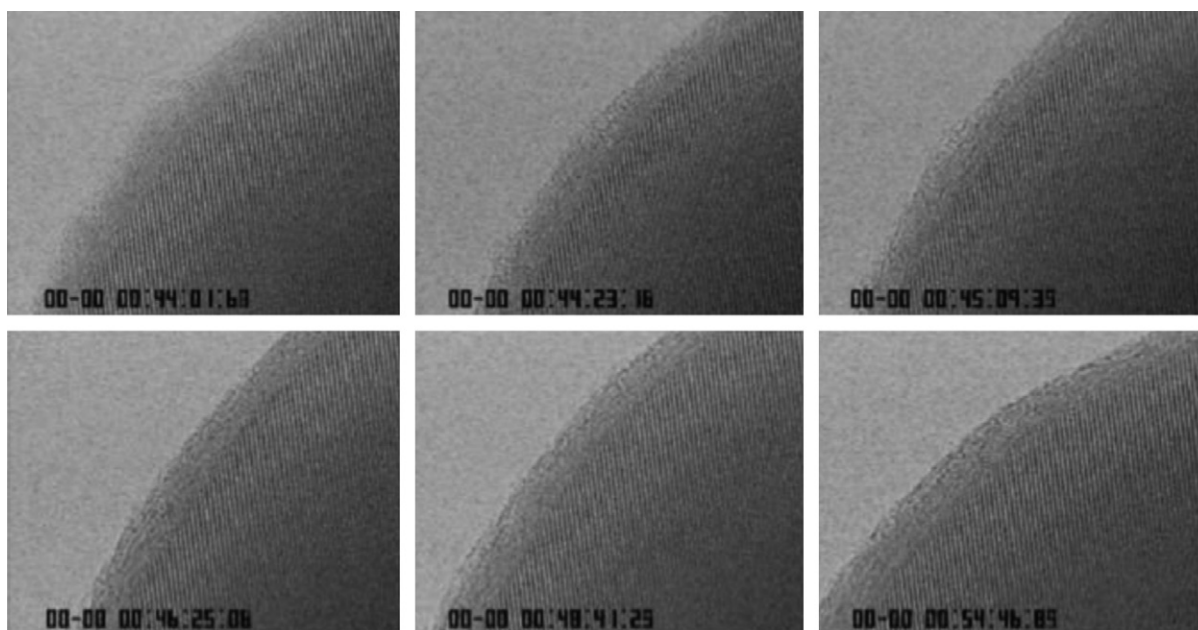


Fig. 6. Captured video images of the surface layer changes to carbon-coated LiFePO₄ during heat treatment at 700 °C under 12 mPa of nitrogen.

with the presence of an amorphous carbon layer at the surface. However, the carbon layer is not as uniform as in the previous experiment, probably because the temperature has not reached 700 °C.

These studies showed that the precursor Fe(0) and the Fe(III) precursor give similar synthesis results. This finding tends to suggest that both Fe(0) and Fe(III) are stabilized to Fe(II) owing to the hydrogenous reducing agent during heat treatment to form C–LiFePO₄. From our studies, the optimum temperature to prepare C–LiFePO₄ is 700 °C, which is the temperature that is also employed to prepare C–LiFePO₄ by some other research groups [22–24]. Moreover, these observations direct us to use low-cost precursors, such Fe(0) or iron oxide with lactose or sugar, for mass production of C–LiFePO₄. The details of the mechanisms were published in our previous papers [20,25].

Because of safety issues with Li-ion batteries for transportation and energy storage applications, a series of observations were conducted to examine the thermal stability of the structure of nano C–LiFePO₄. Recent safety investigations of ‘18650’ Li-ion batteries have shown that, even at low charge-rate C/5, the distribution of temperature is not homogeneous and exceeds locally 200 °C; it can

even be much higher locally, and generate an exothermic reaction at the local state [26]. In case of failure of the battery, the temperature that has been reached is higher than 660 °C, since the aluminium beads on the collector have melted [26]. These features that may take their origin in the Brantly effect [5] result in the need for the active cathode elements to remain stable up to 700 °C. To explore the thermal stability of C–LiFePO₄, a sample synthesized using precursor from method C was examined by in situ STEM up to 900 °C. Fig. 9 shows a sequence of BF-STEM images of C–LiFePO₄ under vacuum using the HD-2700C at low and high magnification, and at increasing temperatures: (a) room temperature (RT), (b) 450, (c) 500, (d) 700 and (e) 900 °C. The left-hand column shows BF-STEM at low magnification. The middle and right-hand columns are BF-STEM images obtained at high magnification. We can observe that under vacuum, the amorphous carbon coating on the LiFePO₄ particles becomes thicker and less uniform at 450 °C than in the case of the experiment performed under the pressure of 12 mPa. A discrete interface region between the amorphous carbon and LiFePO₄ particles is present at the surface at 900 °C, and changes of the LiFePO₄ structure are clearly observed in the high resolution images. Such structural modifications are consistent with the

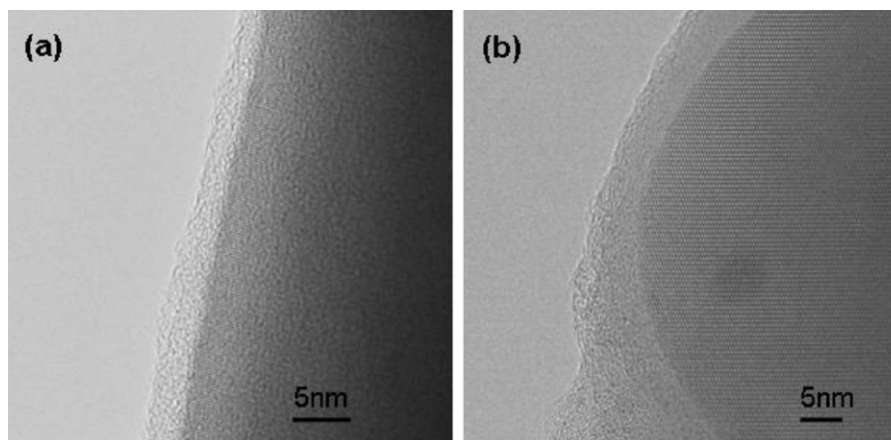


Fig. 7. High resolution micrograph of the C–LiFePO₄ sample at (a) 700 and (b) 750 °C.

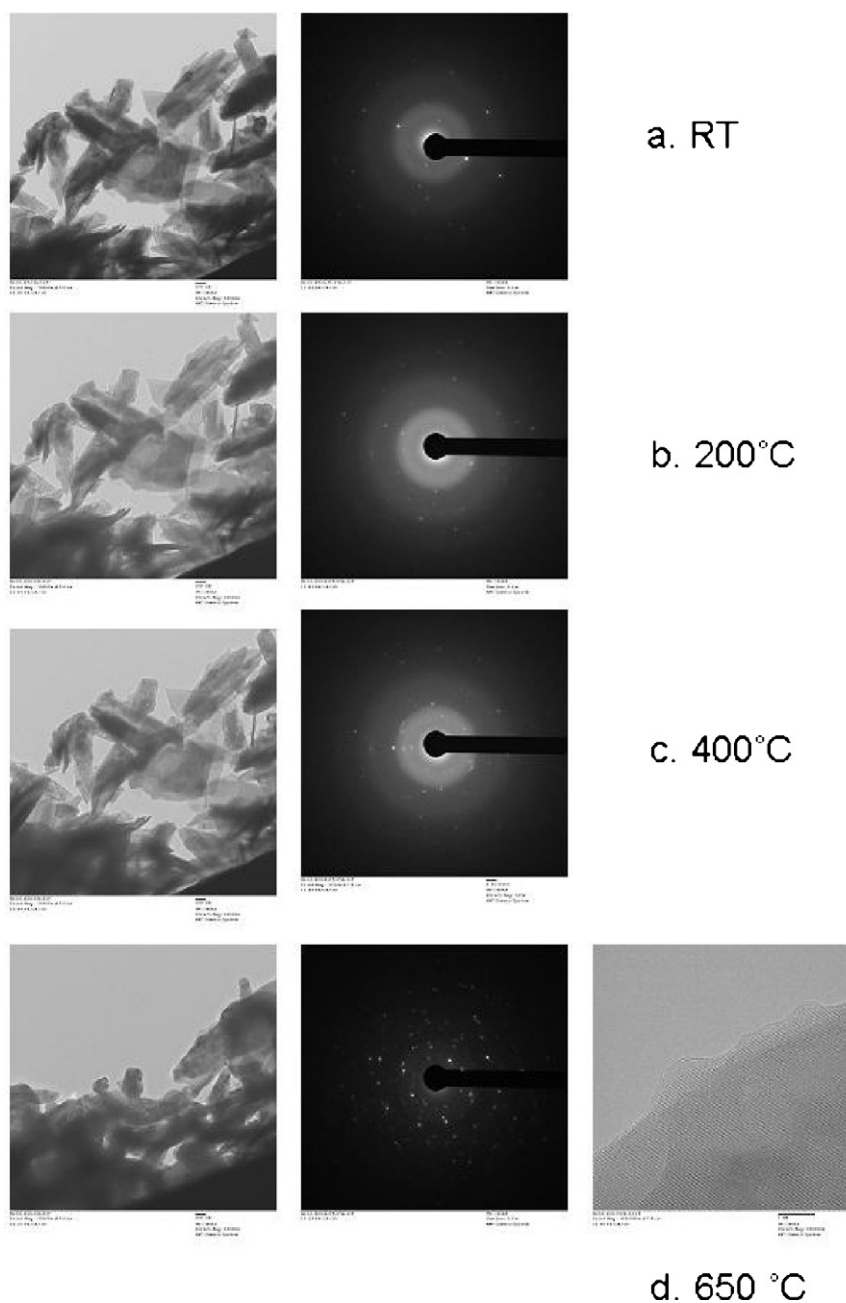
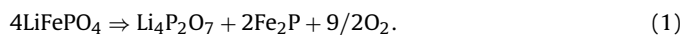


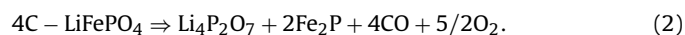
Fig. 8. TEM and electron diffraction patterns of a mixture of Fe, LiOH, H₃PO₄, lactose, at (a) room temperature (b) 200, (c) 400 and (d) 650 °C under 12 mPa of nitrogen.

decomposition of LiFePO₄ at temperatures $T \geq 800$ °C, according to the reaction



This decomposition has been observed in prior works on LiFePO₄ heated at 800 °C [27]. A variant of this decomposition has been proposed [28]. Fig. 10 reproduced from this earlier work is a plot of change in standard free energy for reactions as a function of temperature. Two key characteristics of Ellingham diagrams are: (i) all metal oxide (oxidation of metal to metal oxide) curves slope upwards, and (ii) the position of the line for a given reaction on the Ellingham diagram shows the stability of the oxide as a function of temperature. A given metal can reduce the oxides of all other metals whose lines lie above it on the diagram. Since carbon oxidation to CO has a negative (downward) slope, carbon can then reduce metal oxides to metal. Based on the Ellingham diagram presented in

Fig. 10, the maximum stability of carbon-coated LiFePO₄ is around 750 °C. When the temperature is higher than 750 °C, decomposition of C–LiFePO₄ is expected to occur according to predictions from the diagram, according to the reaction



The difference between Eqs. (1) and (2) is that Eq. (2) implies a predominant role of the carbon. Since the carbon does not penetrate into LiFePO₄, however, this reaction can occur only at the interface, and since the interface is sharp, the decomposition should concern only few atomic layers. However, the LiFePO₄ particles heated at 800 °C in [16] were not intentionally carbon-coated. Since, however, carbon was present in the chemical formula of the precursors used for the synthesis, we cannot preclude that the particles of the final product were non-intentionally carbon-coated. Nevertheless, the amount of Fe₂P was so large that it could be detected by X-ray

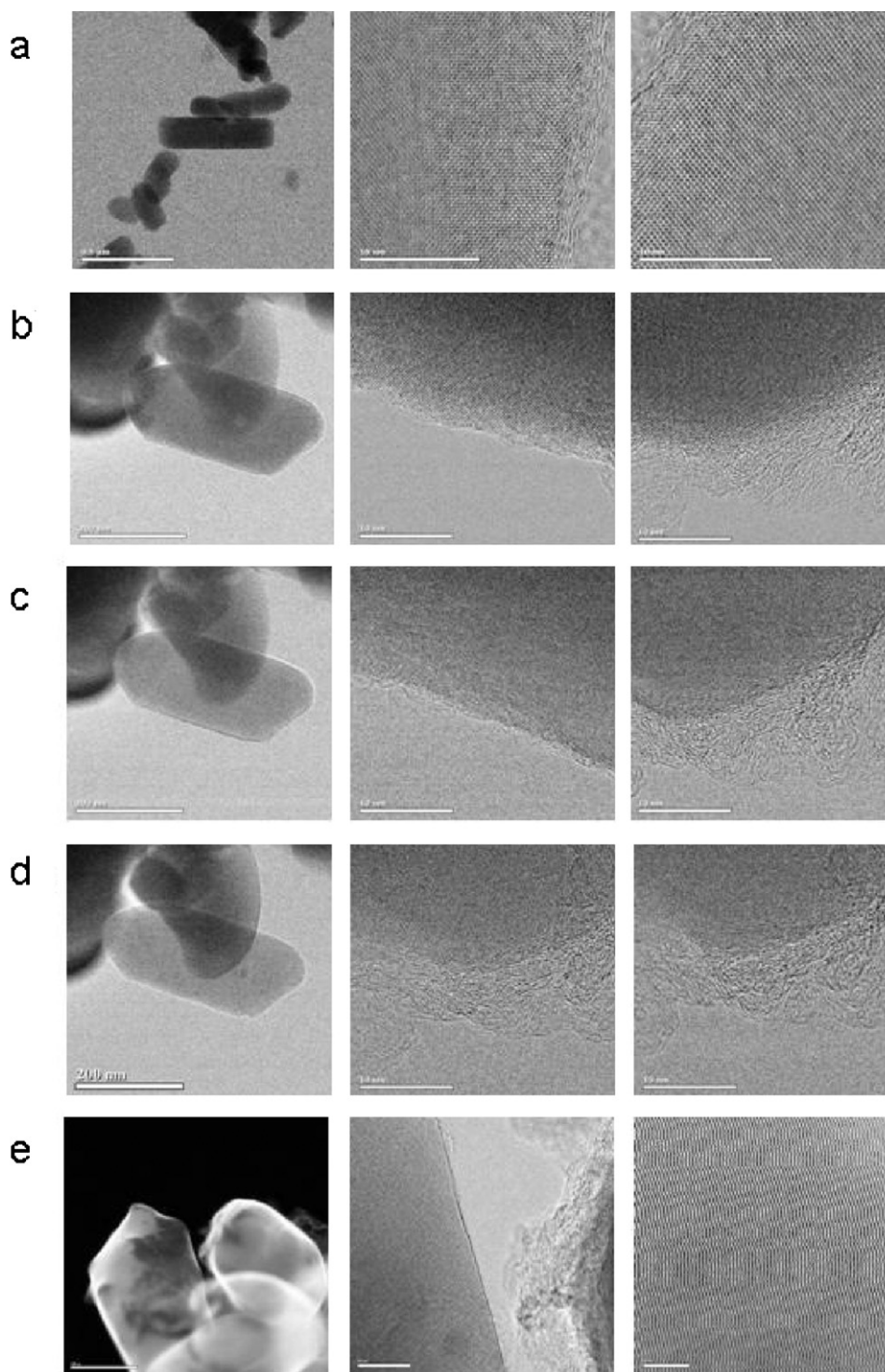


Fig. 9. Sequence of STEM images, at low and high magnification, obtained during heat treatment of carbon-coated LiFePO_4 under vacuum at (a) RT, (b) 450, (c) 500, (d) 700 and (e) 900 °C.

diffraction; this is not compatible with the formation of Fe_2P only at a sub-nanometer layer at the interface between a hypothetical carbon coat and the LiFePO_4 . In addition, the magnetic measurements have shown that Fe_2P is formed under the form of nanoparticles, which opposes a more or less uniform distribution of Fe_2P under the form of a layer. We also note that the formation of such nanoparticles is indeed observed in the in situ TEM images. Therefore, the results obviously favour the hypothesis that the presence of Fe_2P is linked to the decomposition of LiFePO_4 according to Eq. (1), whether the

particles are carbon-coated or not. In any case, we find that these decomposition effects occur only at $T \geq 750$ °C, and the stability condition is that the sample should not be heated above 700 °C, as already mentioned above.

The effects of the processing conditions on the electrochemical performance of C- LiFePO_4 were investigated galvanostatically at C/24 rate. The results obtained in the first cycle with C- LiFePO_4 prepared by methods A, B and C are presented in Fig. 11. The procedure for method A and B is a one-step process to made

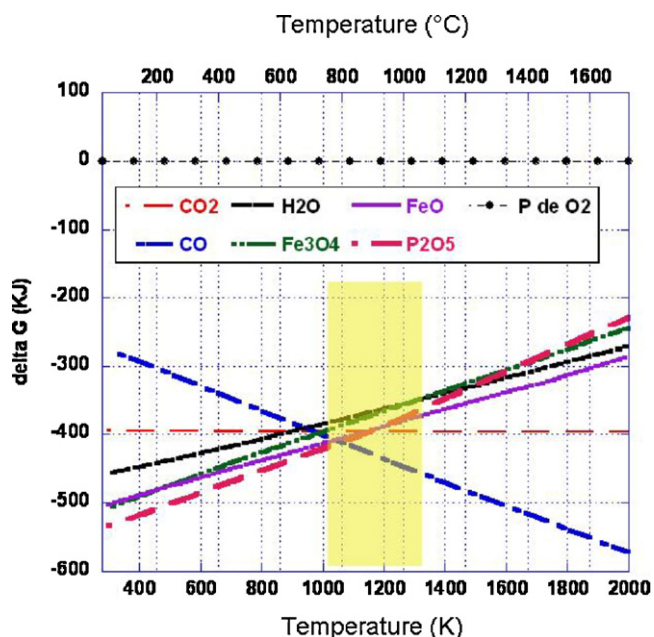


Fig. 10. Ellingham diagram and instability domain of C-coated LiFePO₄ (in yellow rectangle). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

carbon-coated LiFePO₄, and method C (hydrothermal process) is a two-step process, which is a more costly compared to the other methods. The reversible capacity is higher when method C is used (157 mAh g⁻¹), and the reversible capacity is comparable between method A (148 mAh g⁻¹) and method B (145 mAh g⁻¹). According to the cost–performance relationship, method B that uses Fe(0) is the most attractive for mass production of carbon-coated LiFePO₄.

Another question that is still pending is the exact role played by the carbon coat, besides the role of conducting the electric current for which it has been introduced [2]. In particular, the results reported in the present work shows unambiguously that the interface between carbon and LiFePO₄ annealed at 700 °C for 45 mn is sharp, and that the surface layer is very well crystallized, while uncoated particles are known to have a surface layer which is severely disordered [4]. Nevertheless, it was not possible so far

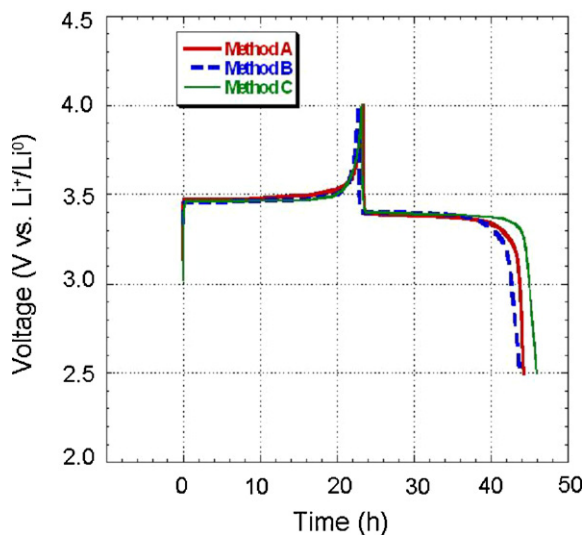


Fig. 11. First charge–discharge cycle at C/24 of C–LiFePO₄/Li cells. Electrolyte, LiPF₆ + EC + DEC. C–LiFePO₄ prepared by (a) method A, (b) method B and (c) method C.

to determine unambiguously whether the re-crystallization of the surface layer is due to the annealing at 700 °C, or it is due to the interaction of the carbon with the iron, which is known to be important in biological processes and at the surface of Fe-bases ferrites [4] as well. To make a distinction between these two effects, we have made the same in situ TEM studies on LiFePO₄ without carbon coating. The STEM images of the sample at room temperature are shown in Fig. 12. They show the non-spherical shape of particles that is characteristic of the particles prepared by hydrothermal process (see also Ref. [29]). At higher magnification in Fig. 13, we observe that a disordered surface layer, about 7–10 nm thick, surrounds the well-crystallized core region. The sample is heated up to 750 °C, at the same heating rate as in the previous experiments (see Fig. 2). Nothing changes up to 600 °C, where the thickness of the disordered layer reduces to circa 6.5 nm during the heating process. When arriving at 700 °C at the rate shown in Fig. 2, the thickness of the layer has still be reduced, as it can be seen in Fig. 14. When the temperature is stabilized at 700 °C, the thickness of the disordered surface layer is reduced to 3.5 nm after 8 mn, and 2.7 nm after 16 mn. We then observe the same low dynamics observed on the carbon-coated sample at the same temperature. To accelerate the dynamics, the sample has been heated to 750 °C. At this temperature, the surface layer has disappeared and the sample is well crystallized up to the surface, as it can be seen in Fig. 15. This well crystallized surface remains stable upon cooling to room temperature.

These results show that the cure of the surface disorder at 700 °C is an annealing effect. The correlation between this annealing effect on the surface of the uncoated particles and the deposit of a homogeneous carbon layer at the same temperature with comparable slow dynamics gives evidence that it is the homogenization of the surface forming a well crystallized LiFePO₄ layer under the annealing effect that allows for the deposit of an homogeneous carbon layer at this temperature. Therefore, the disordered surface layer observed in the samples that have been prepared by hydrothermal process comes from the fact that the temperature reached in the synthesis process is much smaller than 700 °C. Usually, with the hydrothermal route, the synthesis of C–LiFePO₄ is a two-step process. The uncoated LiFePO₄ is synthesized first, at temperature much smaller than 700 °C, the reason for the presence of a disordered surface layer at the surface of the particles. In a second step, the carbon precursor is added to the LiFePO₄ powder upon heating at 700 °C. This heating at 700 °C is actually needed for two reasons. One that we had already mentioned is that heating at this temperature is needed to obtain a coating with a conductive form of carbon [30]. Another one is that this temperature is needed to re-crystallize the surface layer, and correlatively obtain a uniform and homogeneous carbon deposit.

To investigate the impact of the crystallization of the surface layer evidenced in Fig. 15 on the electrochemical properties, we have reported the first charge/discharge of a battery in Fig. 16 obtained under the same conditions as in Fig. 12, in which the active cathode element was non-coated LiFePO₄, before and after heating at 700 °C during 4 h for comparison. The same powder (particles of average thickness 40 nm) was used to avoid any size effect of the particles on the electrochemical properties. The experiments were performed at rate C/12. The results show that the capacity of the cell prepared with non-coated LiFePO₄ before heating at 700 °C is very small and actually negligible. With LiFePO₄ that has been heated at 700 °C, the capacity has improved, which is the effect of the crystallization of the surface layer of the LiFePO₄ particles observed in Fig. 14. However, the capacity only reaches ca. 44% of its theoretical value, while, after carbon coating, the capacity of these particles is close to the theoretical value. This is indeed the evidence that, even in the case of nano-scaled particles, the carbon coating alone is far from sufficient to recover the full capacity of C–LiFePO₄, for the reasons we have recalled in Section 1.

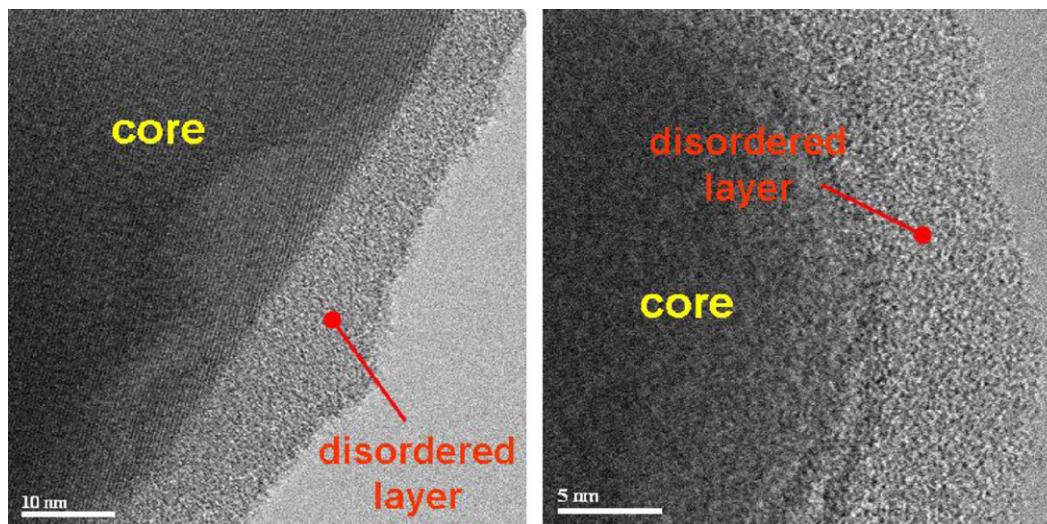


Fig. 12. STEM images of the uncoated LiFePO_4 sample at room temperature.

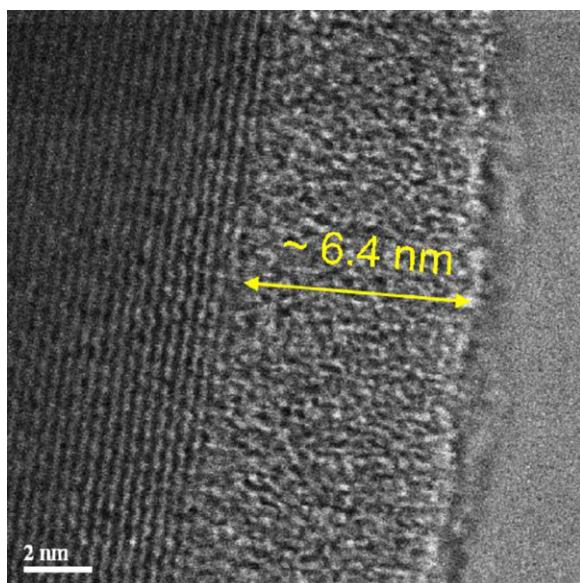


Fig. 13. Same STEM images as in Fig. 12 with higher magnification showing the disordered surface layer, the thickness of which is indicated in the figure.

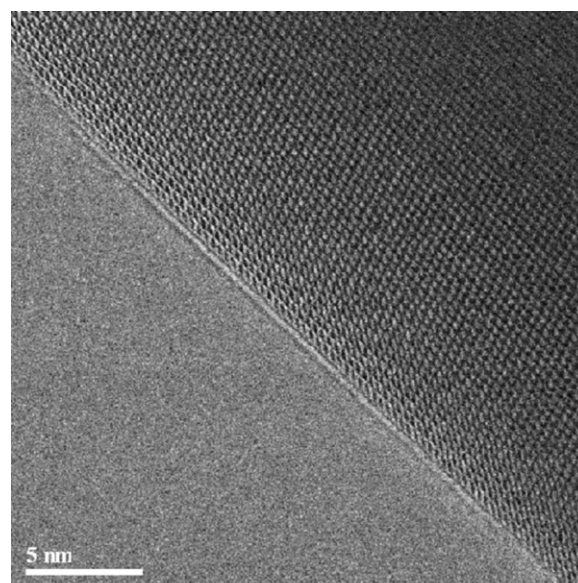


Fig. 15. STEM images of the uncoated LiFePO_4 sample at 700 °C. There is no longer any surface layer.

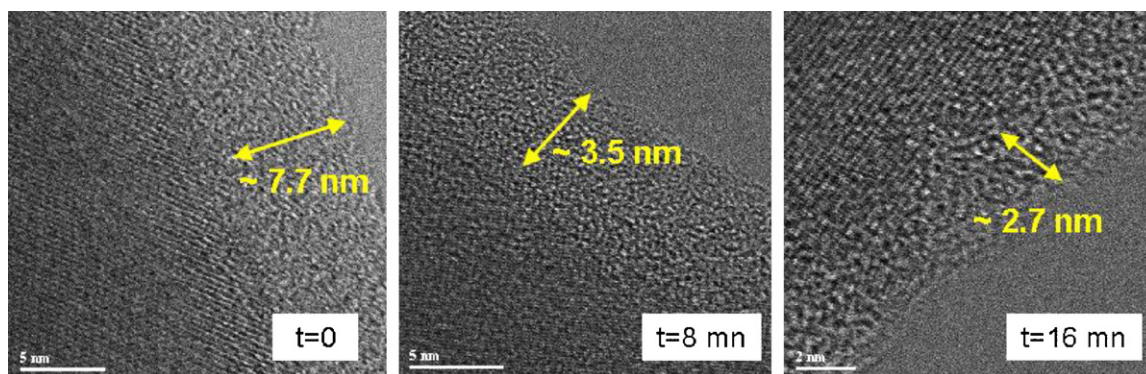


Fig. 14. STEM images of the uncoated LiFePO_4 sample at 700 °C at three different times $t=0$ min, 8 and 16 min after this temperature has been reached upon heating the sample according to Fig. 2. The thickness of the disordered layer is indicated in the figures and decreases with time.

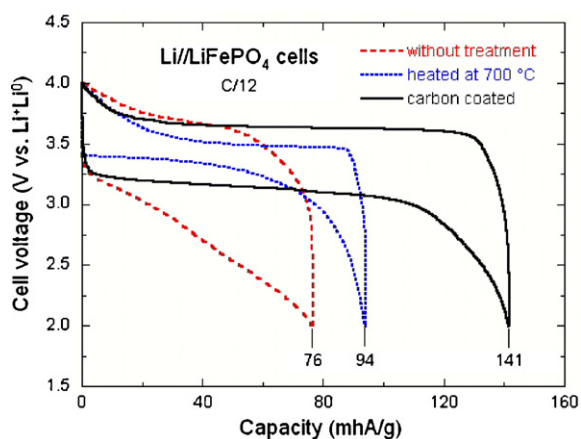


Fig. 16. Electrochemical profiles at C/12 of LiFePO₄/Li cells. Electrolyte, LiPF₆ + EC + DEC. LiFePO₄ positive electrodes were (a) non coated, non annealed (b) heated at 700 °C, non coated (c) after carbon-coating.

To understand the fact that the structural ordering of the surface layer has only a small effect, we note that the electrochemical performance of carbon-coated amorphous FePO₄ and chemically lithiated amorphous FePO₄ and crystallized LiFePO₄ particles are comparable [31]. The exposure to humidity induces a delithiation of the surface layer [32]. Note that we have observed a degradation of the electrochemical performance, which might be due to the coat of the particles with lithium oxide and lithium carbonate that have been formed at the surface as a result of the extraction of Li from the surface layer [32]. However, in the present case, the samples have not been exposed to any humid atmosphere, so that the disorder of the surface layer is not accompanied with any surface contamination. In such a situation, the disordered surface layer of LiFePO₄ should have the same properties as the FePO₄ and chemically lithiated amorphous FePO₄ particles in Ref. [31], which explains that its effect on the electrochemical capacity is small. The main effect of the disorder is the stabilization of the homogeneous phase Li_xFePO₄ in the disordered material responsible for the loss of the plateau at 3.4 V in the charge/discharge profile characteristic of the two-phase system observed with the material crystallized in the olivine structure [31]. This contribution of the surface layer for small particles is also the reason for the reduction of the plateau observed in Fig. 15 in the present work, as it has been explained [5,19]. In the present work, the results of the in situ HRTEM experiments are thus fully consistent with the analysis of the electrochemical properties.

The magnetic properties of Fe³⁺ ions in the delithiated layer of the particles that have been exposed to humidity could be efficiently used as a probe of their local environment [4]. In particular, we have shown that these Fe³⁺ ions undergo a transition from low-spin state before carbon coating to high-spin state after carbon coating. The present work thus corroborates our previous claim that this spin transition was evidence for the crystallization of the surface layer during the carbon coating process.

4. Conclusion

The in situ HRTEM is a new and powerful tool to study the synthesis conditions of new materials for lithium batteries. The in situ studies involved observations of the changes that occurred during heating of samples of precursor materials containing Fe(III) and Fe(0) used to synthesize carbon-coated LiFePO₄. This technique is also very useful to study the stability of materials and to optimize the process for mass production. The results obtained from in situ HRTEM observations are helpful to guide our understanding on how to decrease the energy consumption of the synthesis

furnace and to choose the appropriate and low-cost precursors. The data presented here show that low-cost Fe(0) and a low-cost carbon-containing compound such as lactose are very attractive precursors for mass production of C–LiFePO₄, and that 700 °C is the optimum heating temperature. In order to obtain homogenous carbon-coated (“nano painting”) cathode material, we need to heat the powders for only 45 min at 700 °C, thus resulting in some energy saving and much shorter temperature processing time. The stability of C–LiFePO₄ was also investigated as a function of heating time. An interface region between the amorphous carbon and LiFePO₄ particles is formed at the surface at temperature near 900 °C, and structural changes are observed easily at higher magnification. Such structural modifications are consistent with the fact that at temperatures higher than 800 °C, LiFePO₄ has a tendency to decompose. We should not exceed 750 °C in the procedure to synthesize C–LiFePO₄, in order to avoid the destruction of the structure or to generate unwanted reaction products.

On another hand, below 700 °C, the annealing temperature is not sufficient to obtain the crystallization of the LiFePO₄ surface layer, and the carbon deposit is less homogeneous. The optimum range of temperatures to obtain C–LiFePO₄ composite with high electrochemical performance is thus narrow, namely 700–750 °C.

Finally, the differences observed in the stability of the carbon layer between the heat treatments in vacuum and in a partial pressure of gas clearly show that for some processes, the environmental TEM, which allow high resolution structural imaging with the presence of a gaseous atmosphere (such as nitrogen in the present studies) in contact with the sample, constitutes a much better tool for in situ HRTEM because the atmosphere is more realistic for mass production of C–LiFePO₄.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2011.04.003.

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