

SCIENTIFIC REPORTS

OPEN

Aqueous synthesis of LiFePO_4 with Fractal Granularity

Zahilia Cabán-Huertas, Omar Ayyad[†], Deepak P. Dubal & Pedro Gómez-Romero

Received: 28 January 2016

Accepted: 12 May 2016

Published: 03 June 2016

Lithium iron phosphate (LiFePO_4) electrodes with fractal granularity are reported. They were made from a starting material prepared in water by a low cost, easy and environmentally friendly hydrothermal method, thus avoiding the use of organic solvents. Our method leads to pure olivine phase, free of the impurities commonly found after other water-based syntheses. The fractal structures consisted of nanoparticles grown into larger micro-sized formations which in turn agglomerate leading to high tap density electrodes, which is beneficial for energy density. These intricate structures could be easily and effectively coated with a thin and uniform carbon layer for increased conductivity, as it is well established for simpler microstructures. Materials and electrodes were studied by means of XRD, SEM, TEM, SAED, XPS, Raman and TGA. Last but not least, lithium transport through fractal LiFePO_4 electrodes was investigated based upon fractal theory. These water-made fractal electrodes lead to high-performance lithium cells (even at high rates) tested by CV and galvanostatic charge-discharge, their performance is comparable to state of the art (but less environmentally friendly) electrodes.

Lithium ion batteries (LIBs) have revolutionized portable electronic devices in the past two decades, and are primed to make a great impact on transportation technology by powering electric vehicles (EVs). However, this new application demands that LIBs offer higher energy and higher power capabilities at a lower cost and with environmentally friendly materials¹. Since the seminal work of Goodenough and col.², lithium iron phosphate (LiFePO_4) has been researched as cathode material for LIBs thanks to its low cost, abundant raw materials, safety, low toxicity, structural stability and excellent electrochemical properties. The active material can be reversibly charged and discharged with a stable voltage profile at 3.45 V vs. Li^+/Li with a very small change in unit cell parameters during the $\text{LiFePO}_4/\text{FePO}_4$ phase transition. On the other hand, for the development of high power batteries based on this material, it is essential to understand and overcome the factors limiting lithium transport through the electrode. Indeed, despite its high theoretical specific capacity (170 mAh/g) and long cycling lifetime, the high-rate performance of the raw LiFePO_4 is restricted by its poor electronic conductivity (10^{-9} S/cm) and slow lithium diffusion³. Many different approaches involving surface coating have been tried to improve the capacity and rate performance of LiFePO_4 as cathode for LIBs. Increasing the conductivity by coating the LiFePO_4 surface with carbon⁴ or conducting polymers^{5,6} have been two of the most popular.

In addition to coating, the control of surface microstructure constitutes another general approach towards faster electrode reaction for batteries. Among many possible alternatives, fractal electrode design is proposed as a very promising approach for high-performance batteries, since it greatly improves the surface to volume ratio while providing a high energy-density material with large tap density. Thus, the growth of self-assembled nanoparticles into larger microstructures can provide high surface area for high power and large bulk for high energy density. In addition, mass transfer in LIBs can be improved by spreading the reaction sites throughout the entire volume of the device. Space filling fractal networks can work to ensure that there is efficient charge transfer from a huge effective surface area to a current collector. Last but not the least; a fractal granular microstructure could minimize the internal resistance of the electrode. Recently, micro-sized yet porous LiFePO_4 structures have been reported with high electronic conductivity and fast Li^+ permeation. For instance, Liu *et al.* reported the synthesis of 3D nanoporous spherical LiFePO_4/C material by spray pyrolysis techniques⁷. The 3D conductive carbon coating with interconnected pore networks facilitate both electron transport as well as lithium ion diffusion within the particles, leading to excellent cycling performance and rate capability⁷. However, most of the techniques used to grow fractal structures are based on organic solvents, surfactants and templates which make them less attractive

Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain. [†]Present address: Al-Quds University, Faculty of Engineering, Dept. of Materials Engineering, P.O. Box 20002, East Jerusalem, Palestine. Correspondence and requests for materials should be addressed to P.G.-R. (email: pedro.gomez@icn2.cat)

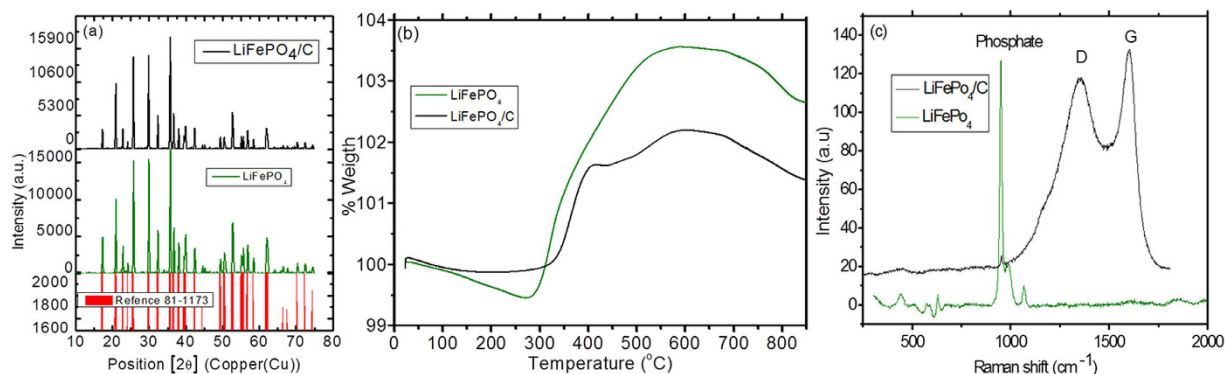


Figure 1. (a) XRD patterns of pristine LiFePO₄ and LiFePO₄/C samples, (b) TGA curves of LiFePO₄ and LiFePO₄/C, (c) Raman spectrum of the LiFePO₄/C.

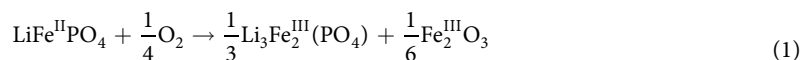
considering production cost of the materials⁸. Therefore the development of effective routes for the synthesis of fractal micro-structured LiFePO₄/C at an ever lower cost still represents a great challenge.

Herein, we are introducing an example of fractal granular LiFePO₄ electrode with excellent electrochemical properties. Briefly, a cost-effective, water-based hydrothermal method is used to prepare micro-nano structured fractal LiFePO₄ materials and electrodes. The samples were fully characterized with different physical-chemical techniques to provide proof of concept. Furthermore, the present work is aimed to investigate the boundary conditions at the electrode surface for lithium transport, and the effect of surface roughness on the diffusion-controlled lithium transport. The surface morphology of the electrodes was examined by AFM and their apparent self-similar dimensions were determined by a triangulation method.

Results

Figure 1(a) shows XRD patterns of pristine LiFePO₄ and LiFePO₄/C samples. All diffraction peaks are indexed to orthorhombic LiFePO₄ (JCPDS card number 081-1173, space group Pnma). It is very important to note that no impurities are detected. This is in contrast with some previous reports on solvothermal syntheses making use of water or organic solvents leading to detrimental impurities⁹. Some researchers reported impurities such as iron phosphides Fe₂P¹⁰ which often form at high temperatures (>600 °C)¹¹ or LiFe(P₂O₇)¹², Fe (II, III) pyrophosphates or phosphates Li₃Fe₂(PO₄)₃¹³ and Li₃PO₄¹⁴. This lack of impurities confirms the suitability of our water-based hydrothermal method for the successful synthesis of pure stoichiometric LiFePO₄ material. Moreover, all diffraction peaks are intense and narrow for our samples, indicating a high degree of crystallinity of the LiFePO₄ phase prepared both before and after carbon-coating.

Figure 1(b) shows TGA curves of pristine LiFePO₄ and LiFePO₄/C composite under flowing air atmosphere. These experiments were carried out to study the thermal stability of the materials and to determine the exact amount of carbon coated on LiFePO₄ active phase. After an initial weight loss associated to loss of water, the TGA curves show a weight gain of 5.0% for LiFePO₄ and 2.4% for LiFePO₄/C between 250–650 °C. The weight uptake of pristine LiFePO₄ can be explained by the following oxidation reaction¹⁵:



The amount of carbon coated on LiFePO₄ was calculated by measuring the difference between the total weight gain of LiFePO₄ and that of LiFePO₄/C and turned out to be 2.6%.

The LiFePO₄/C sample was also analyzed by Raman spectroscopy in order to investigate the nature of coated carbon. As seen in Fig. 1(c), two intense broad peaks were recorded at 1330 cm⁻¹ and 1595 cm⁻¹ corresponding to the A_{1g} vibration mode of the disordered carbon (D-band) and E_{2g} vibration mode of the ordered graphitic carbon (G-band), respectively¹⁶. The ratio of intensities of D-band to G-band (I_D/I_G) is 0.87, indicating sp² carbon, which would enhance the electronic conductivity of the LiFePO₄ material¹⁷.

The chemical composition and valence state of LiFePO₄/C material was confirmed by XPS analysis. Figure 2(a) shows the wide range-scanning spectrum, which consists of Li, Fe, P, O and C components confirming formation of LiFePO₄/C material. The Fe_{2p} spectrum (Fig. 2(b)) exhibits two major peaks (Fe 2p_{3/2} and Fe 2p_{1/2}) at binding energies of 710.9 eV and 724.2 eV indicating Fe(II) valence state which is characteristic of the olivine-type LiFePO₄ products¹⁸. Figure 2(c) shows the deconvolution of the C 1s spectrum in LiFePO₄/C, clearly displaying the lower binding energy featured at 284.6 eV corresponding to C-C carbon and the higher binding energy featured at 286.1 eV followed by a shoulder at 288.9 eV, which was typically assigned to C-O-C, O-C=O arising from epoxide, carboxyl functionalities¹⁹. Figure 2(d) shows the fine structure of C KLL transition, which is strongly affected by the sp²/sp³ configuration. Parameter *D* can be considered as a fingerprint of the type of carbon hybridization, showing values of 13.7 eV for sp² and 21.2 eV for sp³ hybridization states²⁰. For extended carbon phases the *D* value can therefore represent a diagnose of the conducting character of a given material since sp² is associated to graphitic carbons, better conducting than sp³ structures. The *D* parameter value for carbon in our LiFePO₄/C sample turned out to be 16.2 eV which indicates an intermediate composition of sp²

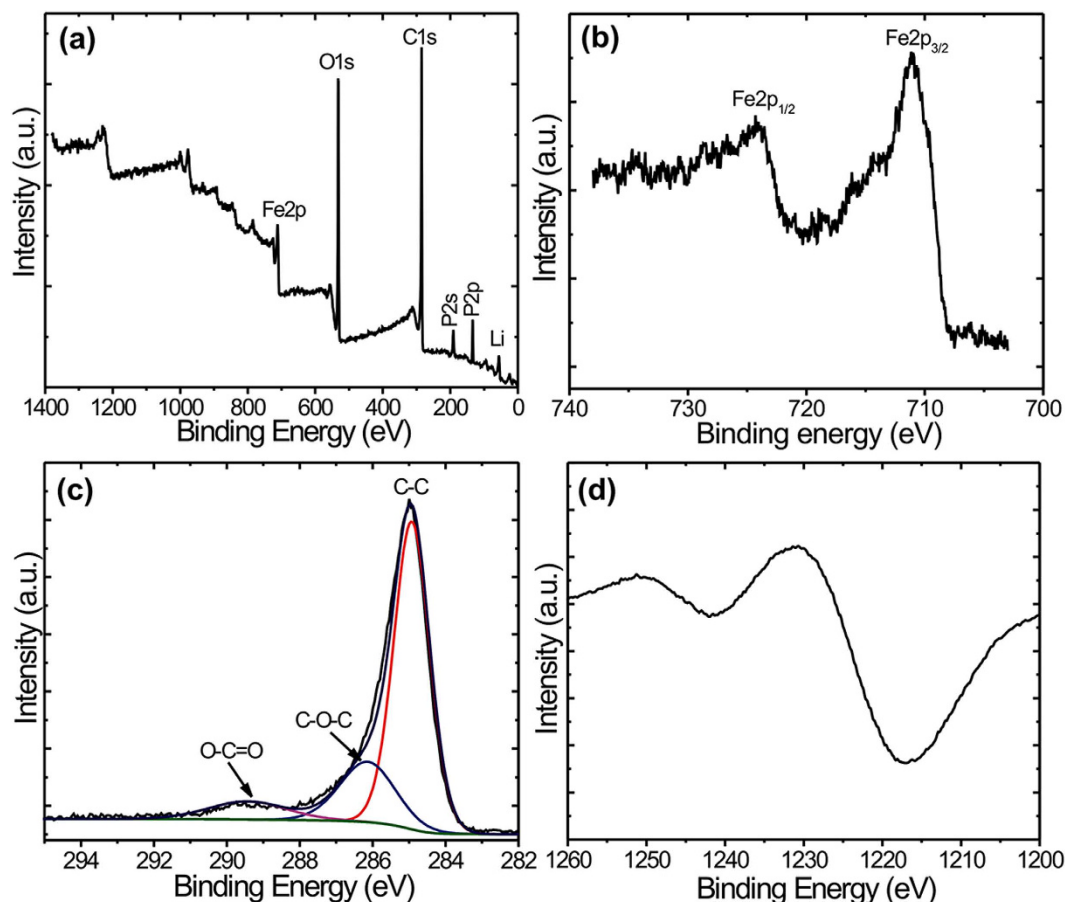


Figure 2. XPS spectra of the LiFePO_4/C powder calcined at 700°C (a) Full spectrum of LiFePO_4/C (b) narrow spectrum of Fe_{2p} (c) core-level XPS spectrum of C_{1s} and (d) Derivate of the carbon auger peak.

and sp^3 , corresponding to a mixture of ca. $2/3$ sp^3 and $1/3$ sp^2 C in the sample. This means that although the carbon coating of LiFePO_4 is not purely sp^2 it does contain enough sp^2 carbon to provide electrical conductivity of the material.

The microstructures of the LiFePO_4 and LiFePO_4/C samples were investigated by SEM and are presented in Fig. 3(a,b). As seen in Fig. 3(a), our LiFePO_4 sample is constituted of large microspheres a few microns in diameter formed in turn by a very large number of nanoparticles of ca. 200 nm in a configuration, which could be described as fractal. Indeed, nanosized primary particles conformed the surface of micro-sized secondary particles form a microstructure reminiscent of the black fractal sketch shown in the Fig. 4. This configuration presents the advantages of nanoparticulate matter and the easy handling and high tap density of microparticles. Inset of Fig. 3(a,b) show details of the closely packed primary nanoparticles featuring inter-particle slit pores. Comparing both of them allows us to conclude that this fractal granularity is retained after the pyrolysis treatment for carbon-coating (Fig. 3b). These results are in contrast to previously reported conventional hydrothermal synthesis of LiFePO_4 which led to very large microcrystals (in air) and required N_2 atmosphere for further growth of smaller particles²¹. In the present work, LiFePO_4 fractal granular geometry is achieved with the simple addition of polyethyleneimine (PEI), which controls the growth of these optimal nano-microstructures without any special treatment.

The samples were also studied with TEM. Figure 3(c,d) compares high-resolution images of pristine and carbon-coated LiFePO_4 primary nanocrystals. From the HRTEM image (Fig. 3c,d), one can clearly see the lattice fringes with an interplanar spacing of 0.34 nm for both LiFePO_4 and LiFePO_4/C nano-particles, which is identified as the characteristic interplanar spacing of the (111) plane of olivine-type LiFePO_4 material. The carbon layer covering the LiFePO_4 surface has an average thickness of 3 nm and is clearly observed in Fig. 3(d). No long-range order is apparent in this carbon layer; yet it must be composed of conducting graphitic carbon (sp^2 according to Raman) comparable to graphene domains (but not diffracting due to its small thickness). Insets of Fig. 3(c,d) show low-magnification TEM images of LiFePO_4 and LiFePO_4/C single crystals, confirming identical nanoparticle morphologies. Moreover, the selected area electron diffraction (SAED) patterns of both LiFePO_4 and LiFePO_4/C (Fig. 3e,f) were indexed as (111) plane confirming the LiFePO_4 orthorhombic structure in agreement with XRD results.

The fractal granularity of LiFePO_4 leads to a characteristic slit porosity formed by the primary nanosized crystals (better seen in the inset of Fig. 3(a,b)). These inter-particle pores extend from the surface to the inner core of the spheres and can facilitate deep penetration of liquid electrolyte solution into the microspheres, thus providing an improved interface contact between the electrode and electrolyte. (supporting information S1).

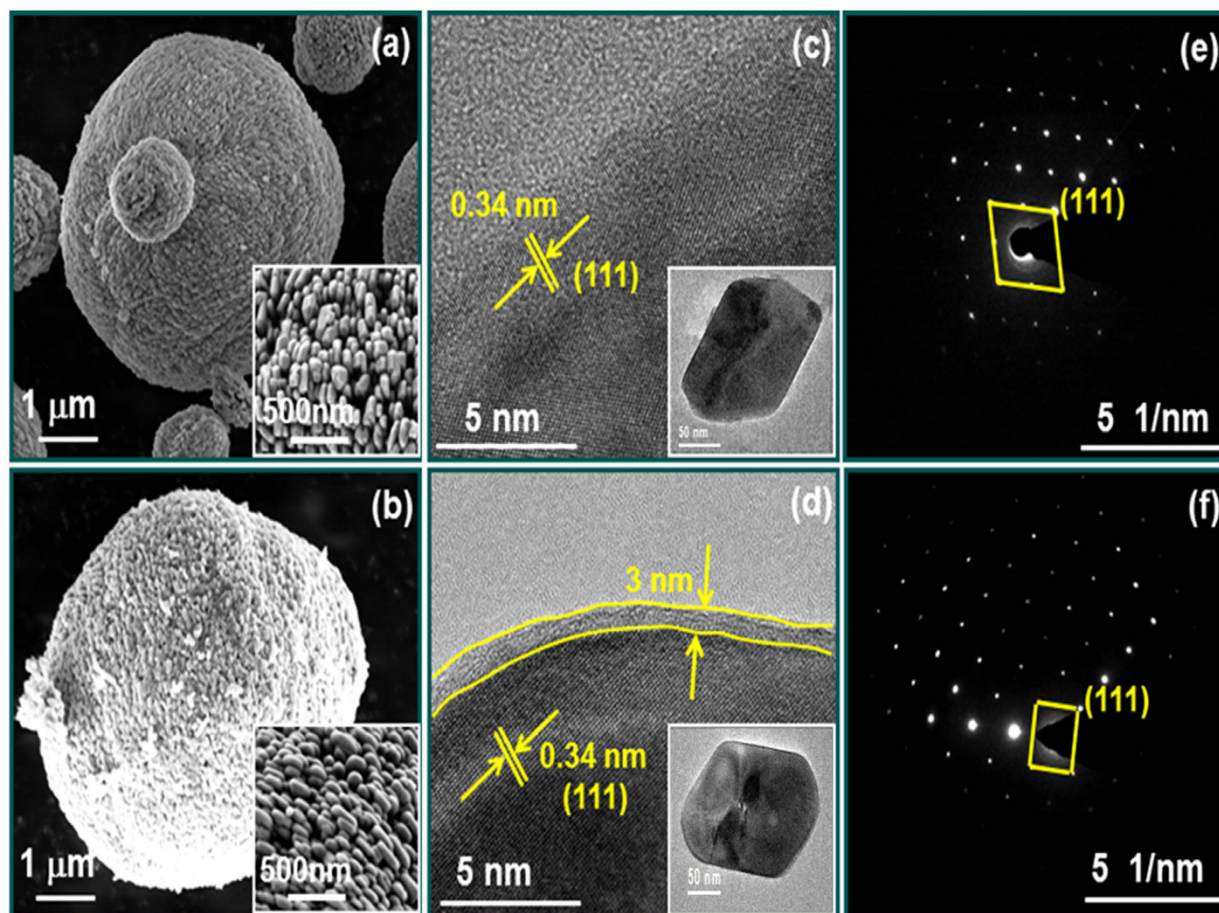


Figure 3. (a,b) SEM images of LiFePO_4 , LiFePO_4/C , inset shows high magnified images. For these two images isolated spheres were selected. Most abundant agglomerates of these secondary spherical particles are shown in Supporting Information 2. (c,d) HR-TEM images of LiFePO_4 , LiFePO_4/C , inset shows low magnified images (e,f) SAED patterns of LiFePO_4 , LiFePO_4/C , respectively.

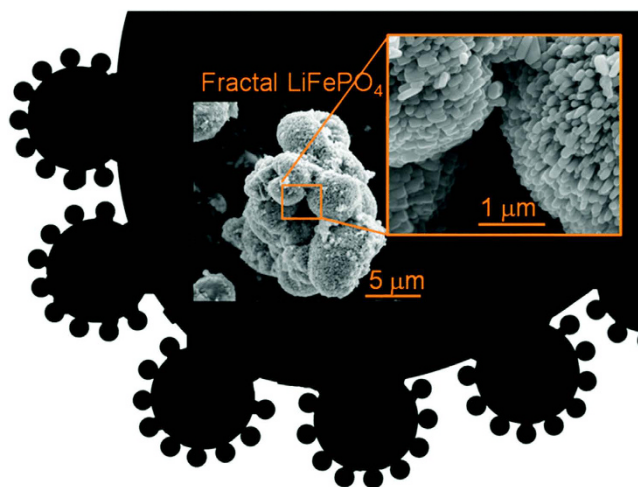


Figure 4. Scheme of LiFePO_4 fractal granularity design.

To further investigate the surface properties of fractal LiFePO_4 material, we performed Brunnauer-Emmett-Teller (BET) analysis of adsorption isotherms shown in Fig. 5(a). The LiFePO_4/C sample shows a typical isotherm of type IV with hysteresis loop in a relative pressure (p/p_0) range of 0.4–1.0, implying the formation of slit-like pores²², a type of porosity which can be easily understood as a result of the stacking of

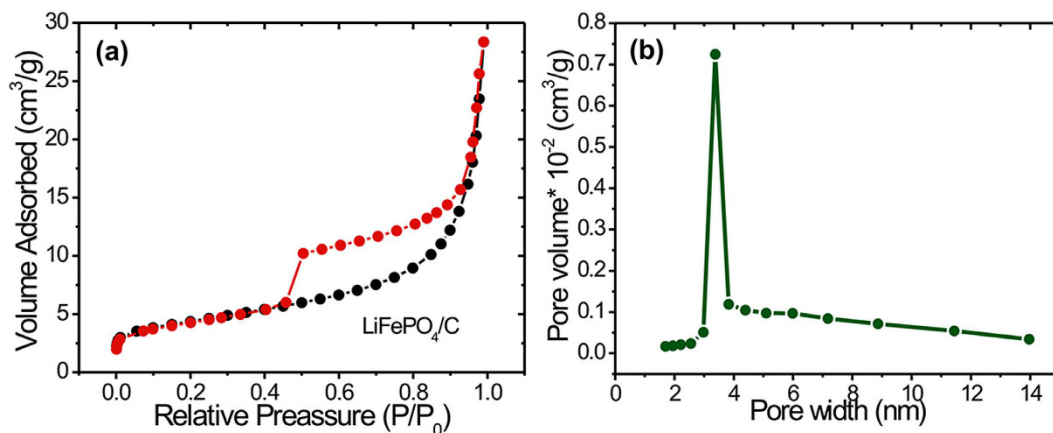


Figure 5. (a) Nitrogen adsorption/desorption isotherms for LiFePO₄/C (b) Barret-Joyner-Halenda (BJH) pore size distribution curve for LiFePO₄/C.

Specimens	Fractal Dimension obtained by AFM	Rms (nm)
LiFePO ₄	2.38	258.0
LiFePO ₄ /C	2.01	207.7

Table 1. Root mean square (rms) roughness and scan size of the LiFePO₄ and LiFePO₄/C electrode determined from AFM images (Fig. 5).

nanoparticles. The measured BET surface area was found to be 14.8 m²/g for LiFePO₄/C. Figure 5(b) shows the Barret-Joyner-Halenda (BJH) pore size distribution curve with a distinct maximum centered at ~3.7 nm. This confirms the mesoporous nature of the LiFePO₄/C fractal structure. The mesoporosity of LiFePO₄/C samples results from a combination of internal space of the agglomerated nanoparticles and microspheres. Despite the modest value of the BET surface area, such a mesoporous structure facilitates diffusion of Li ions from the electrolyte into the electrode bulk by providing short diffusion lengths.

The microstructural characterization of LiFePO₄ was completed with two more complementary techniques, namely AFM (20 × 20 microns) for electrode area analyses and SEM for cross-section (20 microns) analyses. Thus, cross-section SEM images of LiFePO₄ and LiFePO₄/C electrodes coated on Al substrates with elemental composition analyses were carried out and are shown and discussed in supporting information S2 and S3. The film thickness was between 15 μm and 20 μm for LiFePO₄ and 5–10 μm for LiFePO₄/C.

In order to get a better understanding of Li transport and confirm the fractal nature of LiFePO₄, surface roughness was analyzed in triangles of various sizes for a total area of 20 × 20 microns by AFM. Figure 6(a,b) shows AFM surfaces of LiFePO₄ and LiFePO₄/C film electrodes, respectively. It can be noted that the LiFePO₄/C film electrode shows less roughness than LiFePO₄ film electrode. In order to get quantitative insights, root mean square (rms) roughness of both electrodes was evaluated (Table 1). Since these structures appear to be fairly similar on various length scales, this surface can be regarded as a self-similar fractal. The triangulation method, reported elsewhere²³, was used to determine the self-similar fractal dimensions. Figure 6(c,d) gives logarithmic scale dependence of scaled surface area (SSA) on projected triangle size (TS) obtained from the LiFePO₄ and LiFePO₄/C film electrodes, respectively.

For both electrodes, one can find clearly a linear relationship between the log(SSA) and log(TS), indicating the self-similar scaling property of the surface. It is generally known that the self-similar fractal dimension D_{f,ss} of a surface is given in terms of the slope of the straight line 's' (=d log SSA/d log TS) as²⁴

$$D_{f,ss} = -s + 2 \quad (2)$$

From Fig. 6, the outer cut-offs for their fractal structures were found to be 6.5 and 5.5 μm, respectively. Here, it should be stressed that although both LiFePO₄ film electrodes show the self-similar scaling properties, the spatial outer cut-offs for their fractal structures are different from each other.

The electrochemical properties of LiFePO₄ and LiFePO₄/C electrodes were further investigated, results presented in Fig. 7. The ionic diffusion in the self-similar fractal electrode was studied by CV. The sharp oxidation and reduction peaks in CV curves for LiFePO₄/C electrode (see Fig. 7a,b) confirm the excellent reversibility of the Li extraction-insertion reaction as compared to that for pristine LiFePO₄ electrode. The well-defined oxidation and reduction peaks at ca. 3.4 V and 3.6 V are assigned to the Fe²⁺/Fe³⁺ redox couple, corresponding to the Li insertion (Fe³⁺ to Fe²⁺) and extraction (Fe²⁺ to Fe³⁺) in the LiFePO₄ crystal structure, respectively. In contrast, the CV curve recorded for pristine LiFePO₄ is broader and exhibits relatively low current density. This may be attributed to low conductivity and slow Li diffusion in pristine LiFePO₄ electrode.

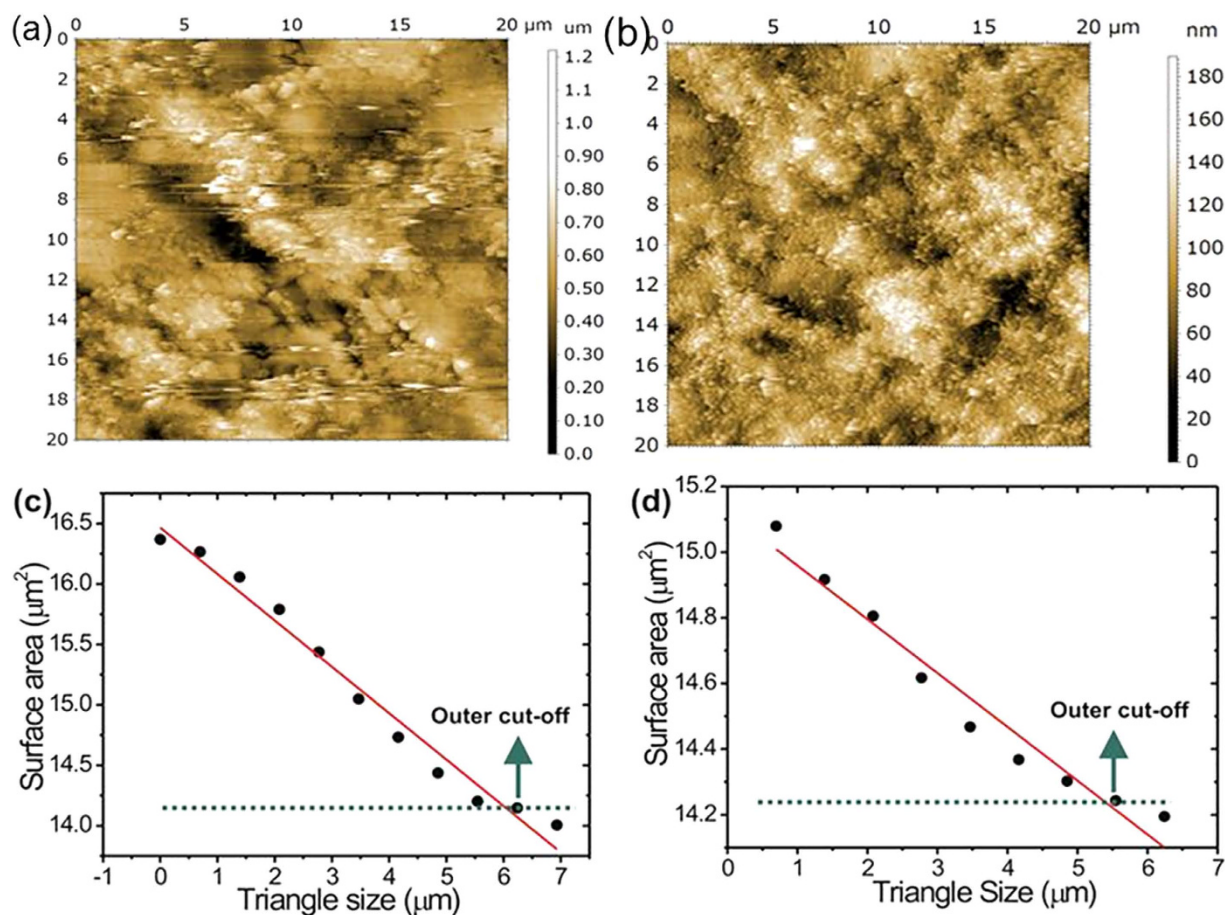


Figure 6. (a,b) AFM images of LiFePO_4 and LiFePO_4/C electrodes, respectively (c,d) Dependence of surface area SA on triangle size TS obtained from AFM images of LiFePO_4 and LiFePO_4/C electrode, respectively. The slope s means $(d \log \text{SSA}/d \log \text{TS})$.

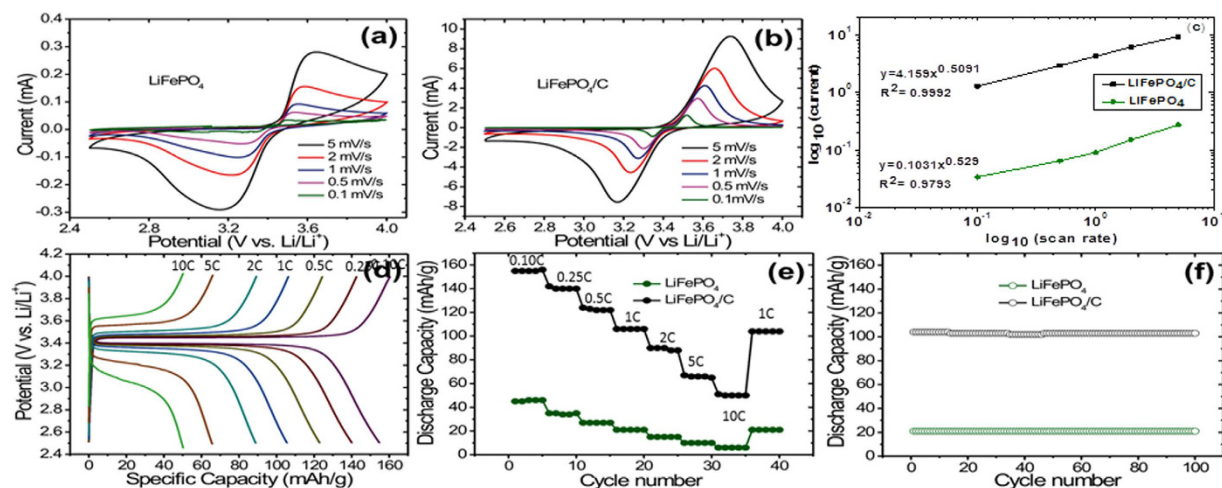


Figure 7. (a,b) Cyclic voltammetry (CV) curves for LiFePO_4 and LiFePO_4/C electrodes at different scan rates, respectively (c) Dependence of anodic peak current I_{peak} on scan rate for LiFePO_4 and LiFePO_4/C electrodes with logarithmic scale (d) Charge/discharge curves at various C-rates for LiFePO_4/C (5th cycle) (e) Discharge capacity at different C-rates of LiFePO_4 and LiFePO_4/C (f) Cycling performance of pristine LiFePO_4 and LiFePO_4/C at 1C.

Strømme *et al.* suggested the peak current method to determine the fractal dimension of a given electrode surface by using cyclic voltammetry: when the recorded cyclic voltammetry current is limited by diffusion of the electroactive species and away from the electrode surface, the fractal dimension d_f of the reaction site on the surface can be obtained by the following equation,

$$I_{peak} \propto v^{\alpha_f} \quad (3)$$

where

$$\alpha_f = \frac{d_f - 1}{2} \quad (4)$$

And I_{peak} is the intensity of the reduction peak, and v is the scan rate. The slope of the plot $\log(I_{peak})$ vs $\log(v)$ is α_f and is called the fractal parameter, which is related to the fractal dimension of the surface as indicated in (4)

Figure 7(a–c) is also used to provide information of the ion diffusion coefficient using an improved Randles–Sevcik equation (see Supplementary Information S4) applicable to fractal electrodes²⁵

$$I_{peak} = \frac{\Gamma(1-\alpha_f)\Gamma(\alpha_f)(\gamma\lambda_0^2)^{\alpha_f-\frac{1}{2}}(nFv)^{\alpha_f}nFAD^{1-\alpha_f}C\chi_{max}(\alpha_f)}{\Gamma(\frac{1}{2})(RT)^{\alpha_f}} \quad (5)$$

where I_{peak} is the peak current, ' Γ ' the gamma function, ' γ ' a geometrical factor close to π^{-1} , λ_0 the length corresponding to the outer cut-off of the fractal electrode, ' n ' the number of transferred electrons per atom, ' F ' Faraday's constant, ' v ' the scan rate, C the concentration of the electrolyte, χ_{max} a dimensionless function of the fractal parameter given in ref. 26, R the gas constant, and T the temperature. ' n ' is equal to 1 since the reaction is



According to equation 4, the diffusion coefficients were found to be 4.11×10^{-14} cm²/s for LiFePO₄ and 1.83×10^{-13} cm²/s for LiFePO₄/C, comparable to previous values found in the literature (6.56×10^{-16} to 0.52×10^{-12})^{27,28}, indicating considerable increases in diffusivity after modifications. This study examines the effects of a carbon coating on the electrochemical performances of LiFePO₄. The effects of the carbon coating as well as the mechanisms for the improved electrochemical performances after modification are discussed based on the diffusivity data and confirm better diffusion in the C-coated sample. The results show that the capacity of bare LiFePO₄ decreased sharply, whereas the LiFePO₄/C shows a well maintained initial capacity.

Figure 7(d) shows the charge/discharge curves at various C rates from 0.1 C to 10 C for LiFePO₄/C cathodes vs. lithium anodes. The LiFePO₄/C exhibits a high specific charge value of 159 mAh/g (ca. 94% of the theoretical capacity of 170 mAh/g) at 0.10 C rate (charge and discharge). This charge at a discharge voltage of 3.4 V and a tap density of 1.70 Kg/L (see below) results in energy density of 920 Wh/L. In contrast, cathodes of the pristine LiFePO₄ do not show a high specific discharge capacity. Even at 0.10 C rate the pristine LiFePO₄ shows a discharge capacity of 45 mAh/g which correspond to 27% of the theoretical capacity. Both samples show good stability at different C-rates (Fig. 7e). The discharge capacity of LiFePO₄/C at 10 C correspond to 31% of the value obtained at 0.10 C, whereas for pristine LiFePO₄ the discharge capacity at 10 C represents 22% of that at 0.10 C (Fig. 7f). The pristine LiFePO₄ cathode material was stable during extensive cycling at 1 C; the capacity retention over 40 cycles is 99%, which is remarkable. Figure 7d shows the very good cyclability of LiFePO₄/C cathode material. This sample was stable over 100 cycles with 98% retention of capacity.

The electrochemical results achieved in the present work are comparable to other reports in the literature, while improving the synthetic procedure with a low-cost water-based simple procedure. For example, Chen *et al.* reported a discharge capacity of 150 mAh/g at 0.1 C rate and 100 mAh/g at 1 C²² for LiFePO₄/C, Yang *et al.* reported discharge capacity of 140 mAh/g for porous graphene/LiFePO₄²⁹ whereas Yu *et al.* prepared template-assisted porous LiFePO₄ particles³⁰ and reported capacity of 140 mAh/g at 0.10 C-rate.

Discussion

In summary, we have developed a low-cost and eco-friendly hydrothermal synthesis of fractal granular LiFePO₄ in aqueous media leading to a pure material, free of the impurities commonly associated to other water-based syntheses. This LiFePO₄ material is composed of 200 nm nanocrystals grown into hierarchically superior spherical microstructures, in turn aggregated into larger units, thus featuring fractal granularity. The size of nanoparticles in fractal micro-structure is tuned by a small amount of polyethyleneimine (PEI) (5%), which plays a triple role as i) reducing agent, preventing oxidation of Fe(II), ii) surface modifier, limiting the growth of individual nanoparticles and iii) as polymer host acting as binder. Moreover, AFM analysis confirms that both electrodes have self-similar fractal nature, although they have different spatial outer cut-offs for their fractal granularity. Carbon coating is also easily and effectively attained without altering the initial fractal granularity of LiFePO₄ electrode. As expected, carbon coating improves the conductivity of LiFePO₄, hence its rate capability and cycling stability as LIB electrode is greatly enhanced. Furthermore, the fractal granularity provides high tap density while maintaining a highly dispersed active material at the nanometer level for an optimized electrode-electrolyte interphase.

Methods

Synthesis of LiFePO₄ fractal design. Fractal LiFePO₄ materials were synthesized through an optimized hydrothermal method. The starting materials were FeSO₄·7H₂O (99%, Sigma-Aldrich), H₃PO₄ (85%, Sigma-Aldrich) and CH₃COOLi·2H₂O (reagent grade, Sigma-Aldrich) and were all used as received. PEI solutions in

water (50 wt%) was also purchased from Sigma-Aldrich, this solution was pre-warmed to 70 °C for faster precursor dissolution. The molar ratio of Fe:P:Li was kept at 1:1:3. In a typical reaction, 6.6618 g of lithium acetate was added to 70 ml of a preheated 5% polyethylene imine solution in water and stirred for 10 minutes. 6.6175 g of iron sulfate was dissolved in 5% PEI (70 ml) and stirred for 2 minutes. Then, 1.65 ml of 85% phosphoric acid was slowly added to the iron sulfate solution, and the resulting solution was stirred for 10 minutes. Finally, both solutions (Li and Fe/PO₄ solutions) were mixed together, stirred for 10 minutes and transferred into 200 ml hydrothermal reactor (Teflon vessel sealed in a stainless-steel autoclave). The reactor was maintained at 200 °C for 24 h. The resulting LiFePO₄ pale green powder was filtered; washed with deionized water/ethanol and dried at 80 °C in a vacuum oven overnight. The final weight of the powder was 3.4932 g, which represents 93% of the theoretical yield.

In the next step, LiFePO₄ particles were coated with carbon using glucose as carbon source. A solution of 10 wt% glucose and 90 wt% LiFePO₄ in water was prepared. This solution was stirred for 5 hours, and then sonicated for 10 minutes. Later, the sample was filtered and dried overnight at 90 °C in a vacuum oven. The sample was initially calcined at 350 °C for 3 h and then sintered at 700 °C for 10 h, all under nitrogen atmosphere. The tap density of LiFePO₄ samples was 1.40 g/cm³ (pristine) and 1.70 g/cm³ (carbon-coated)^{31,32}, which are above the average tap-density values reported in the literature for LiFePO₄^{31,33,34}.

Materials characterization. The phase purity and crystalline structure of the samples were determined by X-ray diffraction (XRD) by means of PANalytical X'Pert PRO diffractometer using a CuK α radiation source ($\lambda = 1.5418$ Å). The morphology of the samples was studied by scanning electron microscopy (SEM, FE Quanta 650 F ESEM) and transmission electron microscopy (TEM, Tecnai G2 F20 HRTEM) operated at an acceleration voltage of 200 keV. N₂ adsorption/desorption was determined by Brunauer-Emmett-Teller (BET) measurements using Micromeritics instrument (Data Master V4.00Q, Serial#:2000/2400). Thermal gravimetric analysis (TGA 500Q) was carried out under air atmosphere between room temperature and 850 °C, and the flow rate of the synthetic air was 10 ml/min. Raman spectra were recorded on a HORIBA Scientific LabRAM HR Raman spectrometer system using Ar laser. The X-ray photoelectron spectra (XPS) analyses were obtained by X-ray photoelectron spectroscopy (XPS, SPECS Germany, PHOIBOS 150). Surface morphologies of the self-affine fractal electrodes were obtained with a SPA 400 equipped with a SPI3800N Probe Station (Seiko Instruments Inc.) in the atomic force microscope (AFM) mode using commercial silicon nitride cantilevers.

Electrode preparation and electrochemical characterization. The cathodes were prepared by pressing a mixture of the active materials with carbon Super P (Timcal) and polyvinylidene fluoride (PVDF) binder in a weight ratio 85:10:5. They were mixed in a mortar for 5 minutes and then dispersed in N-Methyl-2-pyrrolidone and coated onto Al foil. Electrochemical test cells (Swagelok-type) were assembled in an argon-filled glove box with the coated Al disk as working electrode, lithium metal foil as the counter/reference electrode, and 1 M solution of LiPF₆ in a 1:1 vol/vol mixture of ethylene carbonate and diethyl carbonate as the electrolyte. Glass microfiber filter paper was used as separator. For electrochemical battery test, the cells were charged and discharged galvanostatically within a fixed voltage window between 2.5 V and 4.0 V (with identical charge and discharge rates). Cyclic Voltammetry (CV) was performed in the same potential window at a scan rate between 5 mV/s to 0.1 mV/s. All electrochemical measurements were performed with Biologic VMP3 potentiostat/galvanostat.

References

- Armand, M. & Tarascon, J. M. Building better batteries. *Nature* **451**, 652 (2008).
- Padhi, A. K., Nanjundaswamy, K. S. & Goodenough, J. B. Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries. *J. Electrochem. Soc.* **144**, 1188, doi: 10.1149/1.1837571 (1997).
- Xu, Y.-N., Chung, S.-Y., Bloking, J. T., Chiang, Y.-M. & Ching, W. Y. Electronic Structure and Electrical Conductivity of Undoped LiFePO₄. *Electrochem. Solid-State Lett.* **7**, A131, doi: 10.1149/1.1703470 (2004).
- Ravet, N. *et al.* Electroactivity of natural and synthetic triphylite. *J. Power Sources* **97–98**, 503, doi: 10.1016/S0378-7753(01)00727-3 (2001).
- Fedorová, A., Nacher-Alejos, A., Gómez-Romero, P., Oriňáková, R. & Kanišsky, D. Structural and electrochemical studies of PPy/PEG-LiFePO₄ cathode material for Li-ion batteries. *Electrochim. Acta* **55**, 943, doi: 10.1016/j.electacta.2009.09.060 (2010).
- Murugan, A. V., Muraliganth, T. & Manthiram, A. Microwave-Irradiated Solvothermal Synthesis of LiFePO₄ Nanorods and their Nanocomposites for Lithium Ion Batteries. *ECS Transactions* **16**, 49, doi: 10.1149/1.3115307 (2009).
- Liu, J., Conry, T. E., Song, X., Doeff, M. M. & Richardson, T. J. Nanoporous spherical LiFePO₄ for high performance cathodes. *Energy & Environmental Science* **4**, 885, doi: 10.1039/C0EE00662A (2011).
- Yang, J. *et al.* 3D porous LiFePO₄/graphene hybrid cathodes with enhanced performance for Li-ion batteries. *J. Power Sources* **208**, 340, doi: 10.1016/j.jpowsour.2012.02.032 (2012).
- Yu, D. Y. W. *et al.* Impurities in LiFePO₄ and Their Influence on Material Characteristics. *J. Electrochem. Soc.* **155**, A526, doi: 10.1149/1.2919105 (2008).
- Ojczyk, W. *et al.* Studies of selected synthesis procedures of the conducting LiFePO₄-based composite cathode materials for Li-ion batteries. *J. Power Sources* **173**, 700, doi: 10.1016/j.jpowsour.2007.05.055 (2007).
- Ait Salah, A. *et al.* Reduction Fe³⁺ of Impurities in LiFePO₄ from Pyrolysis of Organic Precursor Used for Carbon Deposition. *J. Electrochem. Soc.* **153**, A1692, doi: 10.1149/1.2213527 (2006).
- Kim, D.-K. *et al.* Effect of synthesis conditions on the properties of LiFePO₄ for secondary lithium batteries. *J. Power Sources* **159**, 237, doi: 10.1016/j.jpowsour.2006.04.086 (2006).
- Herle, P. S., Ellis, B., Coombs, N. & Nazar, L. F. Nano-network electronic conduction in iron and nickel olivine phosphates. *Nat Mater* **3**, 147, doi: 10.1038/nmat1063 (2004).
- Arnold, G. *et al.* Fine-particle lithium iron phosphate LiFePO₄ synthesized by a new low-cost aqueous precipitation technique. *J. Power Sources* **119–121**, 247, doi: 10.1016/S0378-7753(03)00241-6 (2003).
- Belharouak, I., Johnson, C. & Amine, K. Synthesis and electrochemical analysis of vapor-deposited carbon-coated LiFePO₄. *Electrochem. Commun.* **7**, 983, doi: 10.1016/j.elecom.2005.06.019 (2005).
- Kim, U. J., Furtado, C. A., Liu, X., Chen, G. & Eklund, P. C. Raman and IR Spectroscopy of Chemically Processed Single-Walled (sic) Carbon Nanotubes. *J. Am. Chem. Soc.* **127**, 15437, doi: 10.1021/ja052951o (2005).

17. Zaghib, K., Mauger, A., Gendron, F. & Julien, C. M. Magnetic studies of phospho-olivine electrodes in relation with their electrochemical performance in Li-ion batteries. *Solid State Ionics* **179**, 16, doi: 10.1016/j.ssi.2007.12.071 (2008).
18. Xiangcheng Sun Caiyun Chen, H. S., Bo, C. & Kai, S. Controlled Preparation and Surface Structure Characterization of Carbon-Coated Lithium Iron Phosphate and Electrochemical Studies as Cathode Materials for Lithium Ion Battery. *International Journal of Materials and Chemistry* **2**, 218, doi: 10.5923/j.ijmc.20120205.06 (2012).
19. Fedorková, A. *et al.* Electrochemical and XPS study of LiFePO₄ cathode nanocomposite with PPy/PEG conductive network. *Solid State Sciences* **14**, 1238, doi: 10.1016/j.solidstatesciences.2012.06.010 (2012).
20. Mezzi, A. & Kaciulis, S. Surface investigation of carbon films: from diamond to graphite. *Surf. Interface Anal.* **42**, 1082, doi: 10.1002/sia.3348 (2010).
21. Kuwahara, A., Suzuki, S. & Miyayama, M. Hydrothermal synthesis of LiFePO₄ with small particle size and its electrochemical properties. *J. Electroceram.* **24**, 69, doi: 10.1007/s10832-008-9442-1 (2010).
22. Chen, R., Wu, Y. & Kong, X. Y. Monodisperse porous LiFePO₄/C microspheres derived by microwave-assisted hydrothermal process combined with carbothermal reduction for high power lithium-ion batteries. *J. Power Sources* **258**, 246, doi: 10.1016/j.jpowsour.2014.02.068 (2014).
23. Annadhasan, A. Methods of Fractal Dimension Computation. *International Journal of Computer Science and Information Technology & Security* **2**, 166 (2012).
24. Shin, H.-C., Pyun, S.-I. & Go, J.-Y. A study on the simulated diffusion-limited current transient of a self-affine fractal electrode based upon the scaling property. *J. Electroanal. Chem.* **531**, 101, doi: 10.1016/S0022-0728(02)01068-9 (2002).
25. Stromme, M., Niklasson, G. A. & Granqvist, C. G. Voltammetry on fractals. *Solid State Commun.* **96**, 151, doi: 10.1016/0038-1098(95)00363-0 (1995).
26. Nicholson, R. S. & Shain, I. Theory of Stationary Electrode Polarography. Single Scan and Cyclic Methods Applied to Reversible, Irreversible, and Kinetic Systems. *Anal. Chem.* **36**, 706, doi: 10.1021/ac60210a007 (1964).
27. Park, C.-K., Park, S.-B., Oh, S.-H., Jang, H. & Cho, W.-I. Li Ion Diffusivity and Improved Electrochemical Performances of the Carbon Coated LiFePO₄. *Bulletin of the Korean Chemical Society* **32**, 836, doi: 10.5012/bkcs.2011.32.3.836 (2011).
28. Satyavani, T. V. S. L., Ramya Kiran, B., Rajesh Kumar, V., Srinivas Kumar, A. & Naidu, S. V. Effect of particle size on dc conductivity, activation energy and diffusion coefficient of lithium iron phosphate in Li-ion cells. *Engineering Science and Technology, an International Journal*. doi: 10.1016/j.jestch.2015.05.011 (2015).
29. Yang, S., Zhou, X., Zhang, J. & Liu, Z. Morphology-controlled solvothermal synthesis of LiFePO₄ as a cathode material for lithium-ion batteries. *J. Mater. Chem.* **20**, 8086, doi: 10.1039/C0JM01346C (2010).
30. Yu, F., Zhang, J., Yang, Y. & Song, G. Porous micro-spherical aggregates of LiFePO₄/C nanocomposites: A novel and simple template-free concept and synthesis via sol-gel-spray drying method. *J. Power Sources* **195**, 6873, doi: 10.1016/j.jpowsour.2010.01.042 (2010).
31. Prosini, P. P. *Iron Phosphate Materials as Cathodes for Lithium Batteries: The Use of Environmentally Friendly Iron in Lithium Batteries*. 85 (Springer-Verlag London, 2011).
32. Oh, S. W. *et al.* Double Carbon Coating of LiFePO₄ as High Rate Electrode for Rechargeable Lithium Batteries. *Adv. Mater.* **22**, 4842, doi: 10.1002/adma.200904027 (2010).
33. Oh, S. W. *et al.* Polyvinylpyrrolidone-assisted synthesis of microscale C-LiFePO₄ with high tap density as positive electrode materials for lithium batteries. *Electrochim. Acta* **55**, 1193, doi: 10.1016/j.electacta.2009.10.007 (2010).
34. Chen, J. Recent Progress in Advanced Materials for Lithium Ion Batteries. *Materials* **6**, 156 (2013).

Acknowledgements

Funding from the E C Seventh Framework program (FP7/2007-2013) under grant Agreement 266090 (SOMABAT) is gratefully acknowledged. ICN2 acknowledges support of the Spanish MINECO through the Severo Ochoa Centers of Excellence Program under Grant SEV-2013-0295. Authors appreciate the award to DPD of a Marie-Curie Fellowship through Beatriz de Pinos Program (BP-DGR-2013) for Catalan system of science and technology, Spain. We thank AGAUR (Generalitat de Catalunya) for project NESTOR Nanomaterials for Energy STORAGE. 2014_SGR_1505.

Author Contributions

Z.C.H., O.A. and P.G.R. designed the experiments and analyzed the data. Z.C.H., D.P.D. and P.G.R. wrote the manuscript. To preparation and reviewing manuscript all authors contributed equally.

Additional Information

Supplementary information accompanies this paper at <http://www.nature.com/srep>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Cabán-Huertas, Z. *et al.* Aqueous synthesis of LiFePO₄ with Fractal Granularity. *Sci. Rep.* **6**, 27024; doi: 10.1038/srep27024 (2016).



This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>

Supporting information

Aqueous synthesis of LiFePO₄ with Fractal Granularity.

Zahilia Caban-Huertas¹, Omar Ayyad², Deepak P. Dubal¹, Pedro Gomez-Romero^{1}*

¹Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain

²Present address: Faculty of Engineering, Dept. of Materials Engineering, Al-Quds

University, P.O. Box 20002, East Jerusalem, Palestine.

Supporting information S1

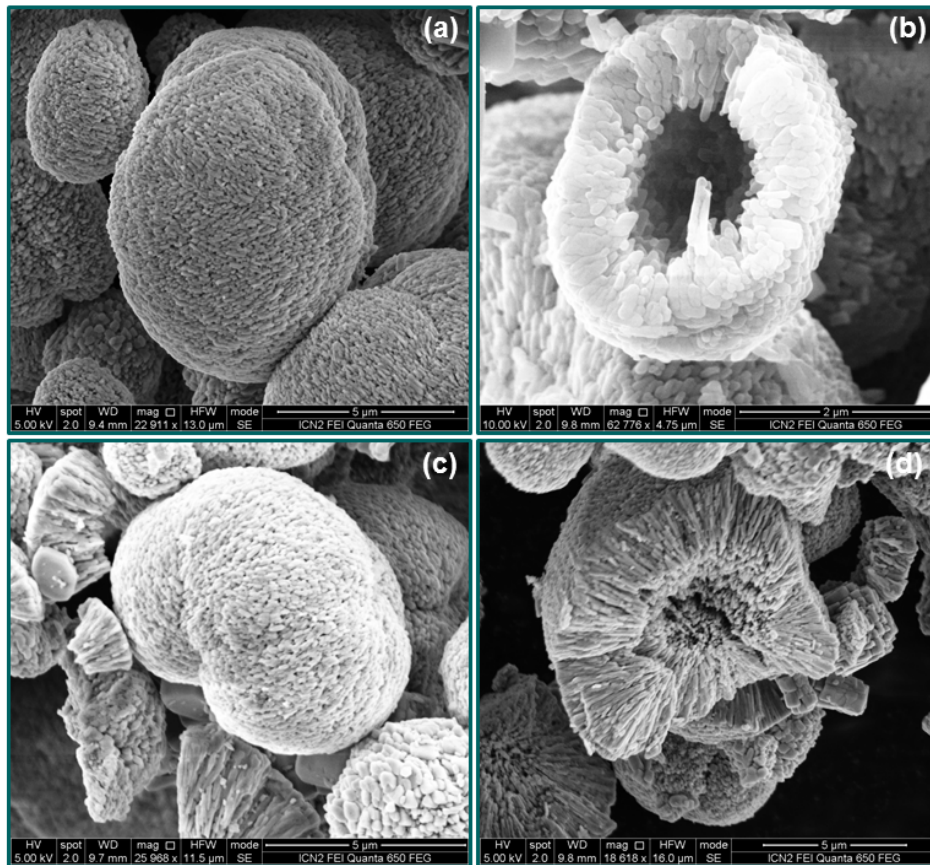


Figure S1 SEM images of (a,d) LiFePO_4 and (b,c) LiFePO_4/C samples, respectively

Supporting information S2

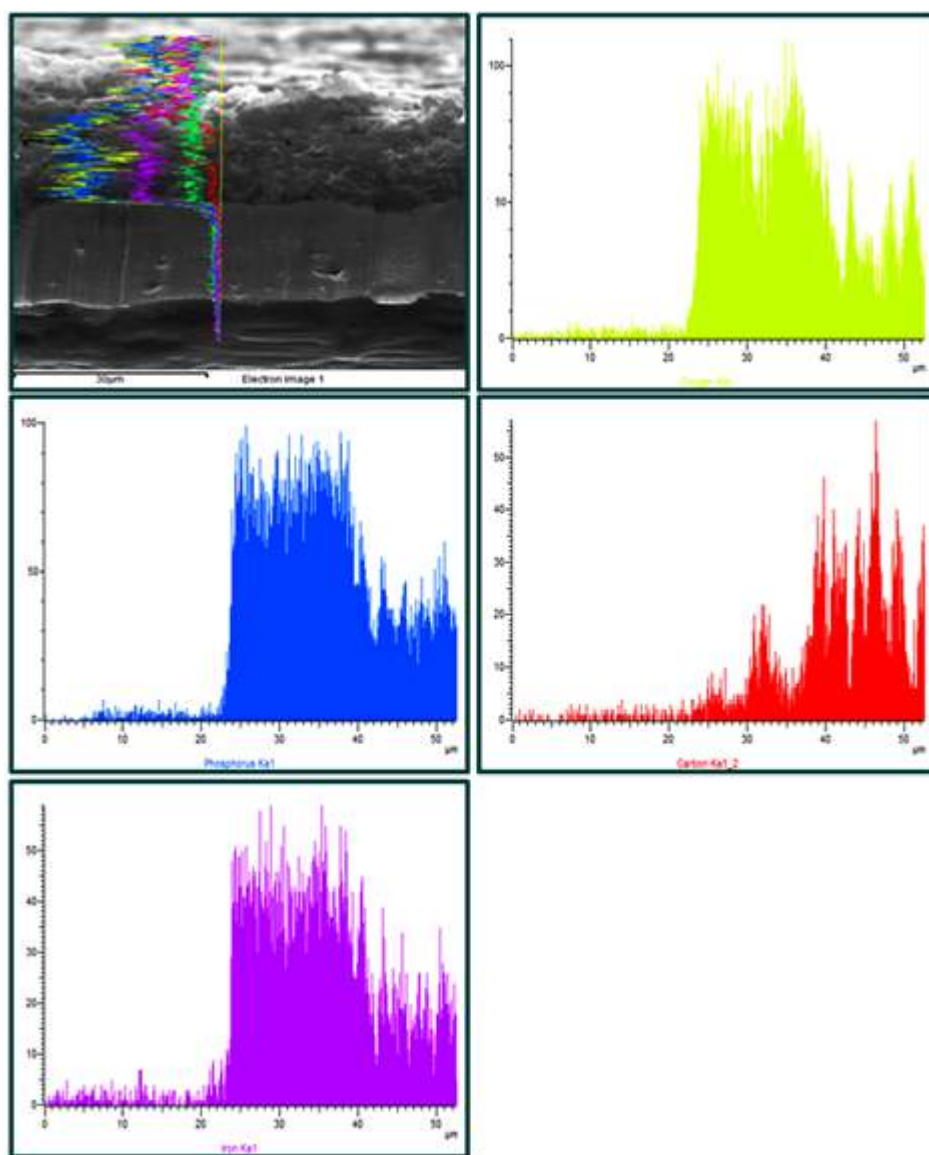


Figure S2 SEM images of the (a) LiFePO_4 electrode and element lining analysis.

Supporting information S3

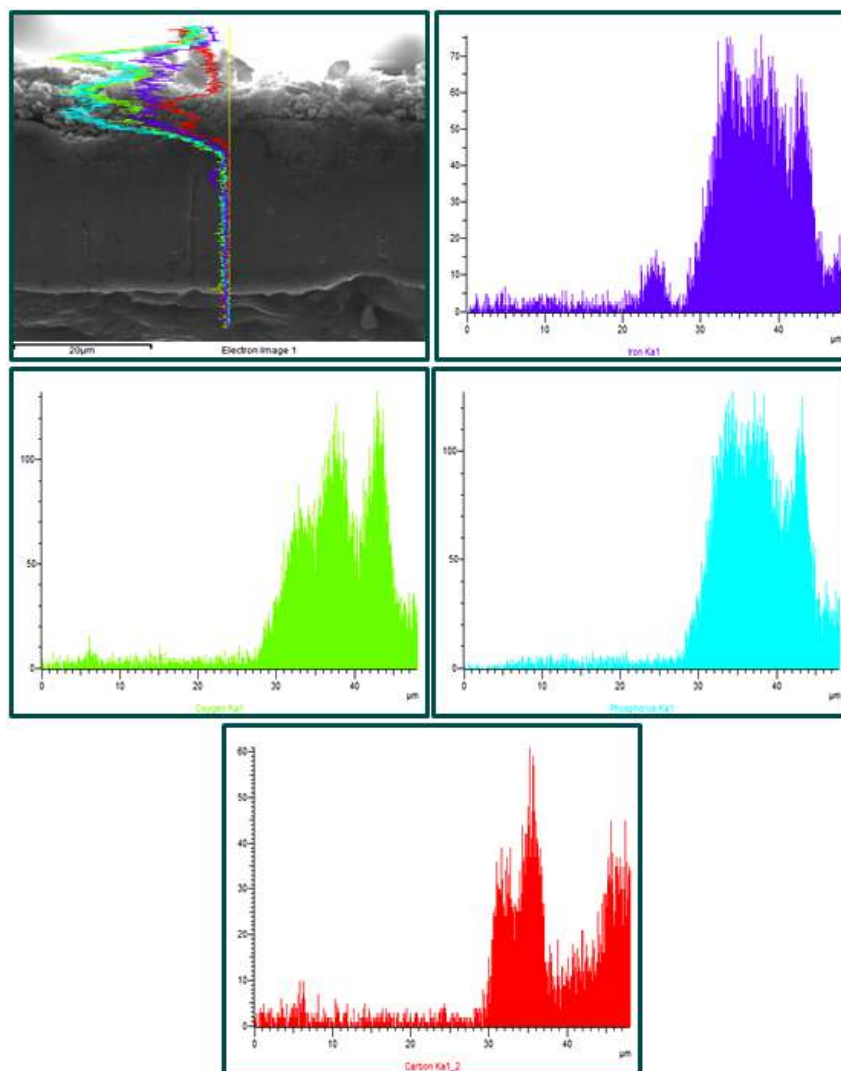


Figure S3. LiFePO₄/C electrode and element lining analysis.

Cross-sectional EDS analyses were carried out for LiFePO₄ and LiFePO₄/C electrodes deposited on Al substrates. The approximate cross-sectional atomic distribution of the C/LiFePO₄ was determined from EDS elements distribution from the top to the bottom of the film. Li cannot be detected by this method due to its low atomic weight. The elements O, P, Fe and C were quite regularly distributed over the surface of Al in both samples.

Supporting information S4

Note on the use of The Randles–Sevcik equation

The evaluation of diffusion coefficients for Li ion battery electrodes is frequently made by using the classical Randles–Sevcik equation

$$I_p = (2.69 \times 10^5) n^{\frac{3}{2}} a D C v^{\frac{1}{2}} \quad (1)$$

This is not always the correct approach, especially for complex microstructures. Indeed it is a common mistake in the LIB literature to use that equation overlooking the strong assumptions made to derive it,¹ namely:

1. Diffusion is one-dimensional from bulk solution towards electrode surface.
2. Electrode surface is ideally smooth.

In lithium battery systems and generally in solid-state electrochemistry diffusion of electroactive species occurs inside the films². It is known that diffusion inside the electroactive film is no longer one-dimensional; instead a complicated three-dimensional diffusion towards accessible active sites for insertion/extraction processes takes place³. Considering the second assumption (smoothness) complex microstructures and in particular fractal ones do have significantly rough surfaces. For rough surfaces, the Randles–Sevcik equation should be modified with new parameters as given in equation (4) in the main text, as proposed by Granqvist and col.⁴

1. Bard, A.J. & Faulkner, L.R. *Electrochemical Methods: Fundamentals and Applications* (Wiley, New York, 2001).
2. Pajkossy, T. & Nyikos, L. Diffusion to fractal surfaces—III. Linear sweep and cyclic voltammograms. *Electrochimica Acta* **34**, 181-186 (1989).
3. Pajkossy, T. & Nyikos, L. Diffusion to fractal surfaces—II. Verification of theory. *Electrochimica Acta* **34**, 171-179 (1989).
4. Stromme, M., Niklasson, G.A. & Granqvist, G.C. Determination of fractal dimension by cyclic I-V studies: The Laplace-transform method. *Physical review. B, Condensed matter* **52**, 14192-14197 (1995).