



Investigation on 3-dimensional carbon foams/LiFePO₄ composites as function of the annealing time under inert atmosphere

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ABSTRACT

The morphological and electrochemical investigation of 3-dimensional (3D) carbon foams coated with olivine structured lithium iron phosphate as function of the annealing time under nitrogen atmosphere is reported. The LiFePO₄ as cathode material for lithium ion batteries was prepared by a Pechini-assisted sol-gel process. The coating has been successfully performed on commercially available 3D-carbon foams by soaking in aqueous solution containing lithium, iron salts and phosphates at 70 °C for 2–4 h. After drying-out, the composites were annealed at 600 °C for different times ranging from 0.4 to 10 h under nitrogen. The formation of the olivine-like structured LiFePO₄ was confirmed by X-ray diffraction analysis performed on the powder prepared under similar conditions. The surface investigation of the prepared composites showed the formation of a homogeneous coating by LiFePO₄ on the foams. The cyclic voltammetry curves of the composites show an enhancement of electrode reaction reversibility by increasing the annealing time. The electrochemical measurements on the composites showed good performances delivering a discharge specific capacity of 85 mAh g⁻¹ at a discharging rate of C/25 at room temperature after annealing for 0.4 h and 105 mAh g⁻¹ after annealing for 5 h.

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1. Introduction

Among the new cathode materials that can replace the presently used transition metal oxide based materials in lithium batteries, the transition metals containing phosphates (LiMPO₄, with M = Fe, Co, Ni, Mn) have gained considerable interest. Since the discovery by Padhi et al. [1], lithium iron phosphate (LiFePO₄) is a promising cathode material due to its good thermal stability, the relatively low costs for synthesis and low environmental impact [2]. However, one of the main drawbacks of olivine LiFePO₄ for the commercial application is its low electronic conductivity and low lithium-ion diffusivity across the LiFePO₄/FePO₄ interface [3] during the charge/discharge processes. Thus, in order to enhance the overall kinetics many efforts have been performed to overcome the problems of poor conductivities of electron and lithium ion by several strategies such as metal-doping, synthesizing fine particles [4,5], and carbon-coating on the LiFePO₄ surface [6–9]. In fact, the carbon coating increases the amount of electrode/electrolyte interface enhancing the charge transport of the lithium ions and conse-

quently improving the electrochemical properties of the lithium ion batteries.

The addition of bi-dimensional (2D) carbon fibers reported by Bhuvaneshwari et al. [10], offered an efficient method for increasing the interfacial area and decreasing the lithium ion diffusion distance, allowing for fast charge transport and improved power capability (specific capacity of 120 mAh g⁻¹ at a charge rate of 0.1C) compared to acetylene black added LiFePO₄ even though the coating was not homogeneous.

Improvements in the battery performance can be achieved by reconfiguring the electrode materials currently employed in 2D batteries into 3D architectures. Improvements in energy per unit area and high-rate discharge capabilities are two of the benefits that may be realized for these 3D cells. Among the different 3D architectures example for charge-insertion batteries [11], the aperiodic “sponge” architecture can be effective. Efficient access of the electrolyte into the electrode pores is essential to harness the advantages that porous electrode materials might offer. Electrode materials with slightly larger pores, mesopores in the range 2–50 nm, also offer high surface areas while potentially avoiding the permanent trapping of lithium ions that is possible with micropores.

The use of commercially available carbon foams as framework for cathode materials offers several advantages: (i) they ensure good inter-particle conductivity, (ii) the continuous macroporous network allows an efficient transport route for the solvated ions

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to get to the mesopores and hence may offer superior battery performances, (iii) the porosity of the carbon foam allows a greater infiltration of the electrolyte into the battery leading to a better electrical contact and (iv) many configurations are possible depending on the particular applications.

These advantages can be used for manufacturing lithium ion batteries. The greatest advantage of lithium ion batteries over the known battery for vehicle application is the attractive energy-density-to-weight ratio. Although a lot of work over LiFePO₄/C composites has been reported in literature, the authors have found a few references [12–14], dealing with the characterization of carbon foams–LiFePO₄ composites. Particularly, Dudney et al. [14] reported an effective capacity use and cycling performance for a cathode composed by graphite foams and LiFePO₄ from slurries and sol–gel process after several hours of annealing. From the experimental data, the authors concluded that the limitations of the battery to date reflect the need to improve the performance of the LiFePO₄ and lithium anode rather than any fundamental limitation due to the graphite foam performance, structure or bonding with the active phase.

Following these indications, in our previous work [15] the preparation of composites of 3-dimensional carbon foams coated with LiFePO₄ prepared by a Pechini-assisted reversed polyol method has been reported. The authors obtained a specific capacity of 85 mAh g⁻¹ (discharging rate of C/25 at room temperature) after annealing the composites at 600 °C under nitrogen atmosphere for 15 min only. The post-annealing treatment is still an important and necessary step in the preparation of Li-ion phosphates. It is performed to avoid secondary reactions but mainly the Fe²⁺/Fe³⁺ reaction which would compromise seriously the efficiency of the product in the cathode material. In the preparation of the LiFePO₄ powders, the annealing process under nitrogen (after reaching the dwell temperature) usually lies in the range of “hours” in dependence upon the process chosen for the preparation.

Following the previous results, in order to improve and to optimize the electrochemical performances we investigated the dependence of the electrochemical performances of 3D carbon foams–LiFePO₄ composites (hereafter CF-LFP) as a function of the annealing time. The electrochemical performances have been discussed in relation to the structural and to the morphological investigation.

2. Experimental

A detailed description of the preparation conditions of the LiFePO₄ samples and of the composites by the Pechini-assisted reverse polyol method has been previously reported [15]. The LiFePO₄ samples are prepared by dissolving Li(CH₃COO)·2H₂O (lithium acetate), Fe(SO₄)₂·7H₂O (iron(II) sulfate) in water as precursors (molar ratio 1:1) with citric acid (2 × mol [Fe]), then adding phosphoric acid in equimolar ratio with Li and Fe ions.

Pure water, due to the rheological properties, favored the infiltration of the ions containing solution into the porous architecture of the foams. The starting solution, with a concentration of the precursors of 0.1 M, was heated up to 80 °C and kept at that temperature for 2–4 h. After cooling down the solution, the product was separated by filtration. Then the precipitate was dried out by heating at 130 °C for 24 h in vacuum. In order to obtain the olivine structured LiFePO₄ phase, the powder was annealed at 600 °C for 10 h.

The commercial foams (GRAFOAM[®] carbon foams, a registered trade name from GRAFTECH International Ltd. [16]) have been cut as disks having 5 mm diameter and 1–2 mm thickness. The composites were prepared by soaking the commercial foams in the starting aqueous solution at 70 °C for 2 h. After soaking, the foams were rinsed slightly with water and dried out by heating at 130 °C for 24 h in vacuum. In order to investigate the properties of the composites as function of the annealing time, the samples were annealed at 600 °C for different times ranging between 0.4 and 10 h.

The structural analysis of the samples was performed by X-ray powder diffraction using a D8 Bruker powder diffractometer (Cu Kα₁ + Cu Kα₂ radiation) with a θ/2θ Bragg-Brentano configuration. The diffractometer is equipped with an energy dispersion detector Si(Li) to minimize the fluorescence effects. A scanning electron microscope Philips XL 30 FEG was used to investigate the morphology of the samples. The X-ray induced photoelectron spectroscopy (XPS) studies have been performed using a PHI 5700 spectrometer equipped with Al Kα (1486.6 eV)

source. Electrochemical studies (e.g. cyclic voltammetry, CV) have been carried out with a multichannel potentiostatic–galvanostatic system VPM2 (Princeton Applied Research, USA). For the measurements, Swagelok-type cells were assembled in an argon-filled dry box with water and oxygen less than 5 ppm. For the powder, a typical cathode material was fabricated as follows: 85 wt.% active material, 10 wt.% acetylene carbon black and 5 wt.% PTFE (60 wt.% water dispersion, Aldrich) as binder were intimately mixed in a few milliliters of 2-propanol and treated in ultrasound bath for 20 min at RT. The resulting paste-like material was cut in pellets and dried out at 60 °C for 24 h under vacuum (resulting electrode containing 20–30 mg active compound). To measure the composites, the foam disks were directly assembled into the cell and a few drops of the electrolyte were added. In the cell, Li metal was used as anode, Powerlyte (1 M LiPF₆ in ethylene-carbonate:di-methyl-carbonate 3:7 (w/w), Ube Industries, Ltd., Japan) as electrolyte, Celgard[®] 2500 as separator. The aluminum current collector was not used. All electrical measurements were performed at room temperature.

3. Results and discussion

3.1. Structural analysis

As previously reported [15], in order to identify the crystalline phase, the XRD reflections of the prepared samples have been compared with those of a commercially available powder used as standard. The spectrum showed the presence of the olivine-like structured LiFePO₄ as major crystalline phase: however, crystalline reflections attributed to secondary phases have been also detected. Although a deeper investigation on the secondary phases has not been carried out, such peaks could belong, possibly, to Fe-poor phases (mostly Li₄P₂O₇) which usually appear during the decomposition of the LFP phase.

3.2. HREM

The important role played by the carbon in the LFP-carbon composites is widely reported in literature. The micrographs in Fig. 1a–c show the morphological surface of the used foams. In the untreated foam, the porous architecture of the foams with hierarchical pore size distribution in micro-, meso-, and macropore ranges can be clearly recognized (Fig. 1a). In the previous work the authors observed the presence of numerous apertures, suggesting that the interior pore system is interlaced and the nanoporous architecture is uniform. While the carbon serves as an electron conductor, the pores, when filled with liquid electrolyte, serve as a source of Li⁺ ions. The importance of a porous nanoarchitecture has been previously reported [11]. The authors emphasize that in this “sponge” approach, the electrolyte layer is formed around a random 3D network of electrode material. This design strategy also represents a concentric configuration in that the electrolyte envelops the electrode material while the other electrode material fills the macroporous and mesoporous spaces. Short transport-path characteristics between the insertion electrodes are preserved with this arrangement.

The micrographs of the CF-LFP composites prepared by soaking before and after annealing at 600 °C for 15 min under nitrogen are shown in Fig. 1b and c. The micrograph shows a very homogeneous coating of the foam surface and consequently a more homogeneous morphology. By soaking, the foam surface is covered by a continuous layer of liquid in which the Li⁺, Fe²⁺ and (PO₄)³⁻ ions are uniformly distributed. The slow evaporation of the solvent leads to a “uniform” layer on the foam surface (Fig. 1b). After annealing under nitrogen for 0.4 h, the formation of a uniform layer of crystalline LiFePO₄ can be observed (Fig. 1c).

The effect of the annealing time on the morphology of the LiFePO₄ crystalline layer is shown in Fig. 2a and b. After 5 h long annealing (Fig. 2a), the layer on the surface of the foam appears to be less “uniform” than after the annealing of 0.4 h. The presence of cracks and voids in the structure of the layer are clearly visible. Such a presence could be explained supposing the occurrence of

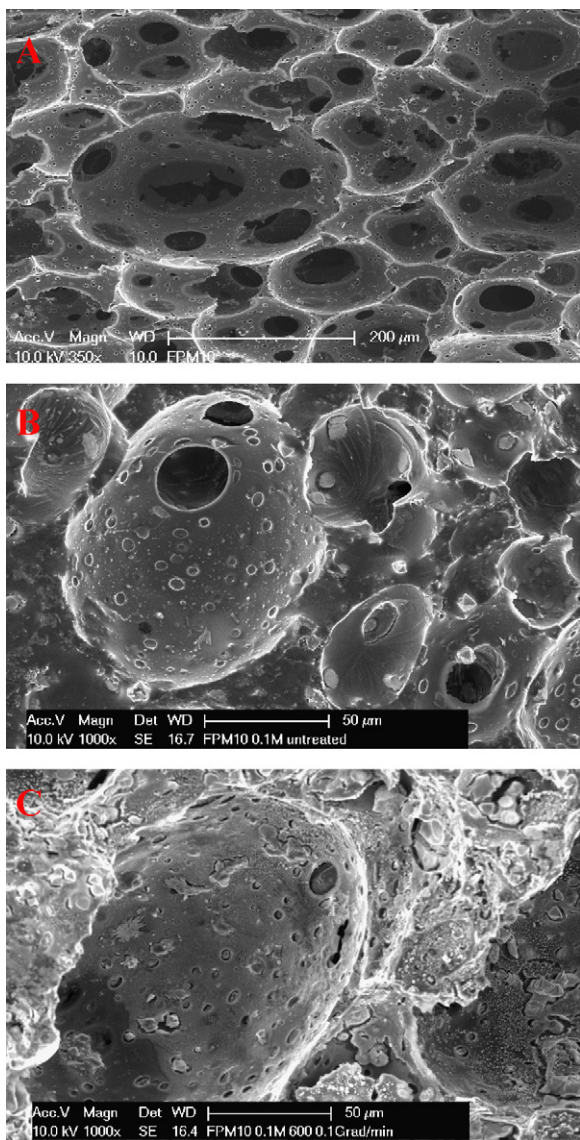


Fig. 1. HREM pictures of (a) carbon foam as delivered; (b) carbon foam–LiFePO₄ composites before annealing at $T=600\text{ }^{\circ}\text{C}$; (c) carbon foam–LiFePO₄ composites after annealing at $600\text{ }^{\circ}\text{C}$ for 0.4 h prepared by soaking.

two events: on one side, a multidirectional growth of the LiFePO₄ crystalline phase occurring during the annealing, on the other side the “cage effect” of the sponge architecture opposing the growth. The mechanical stress arising from these two effects could cause the cracks and the voids. This effect is even more visible after annealing for 10 h as shown in Fig. 2b. The further growth of the LiFePO₄ crystalline phase has brought to the “deformation” of the thin walls inside the porous architecture of the foams with partial or total break-downs of the LiFePO₄ crystalline phase from the foam walls.

3.3. XPS analysis

XPS analysis has been carried on uncoated, coated foams (after annealing at $600\text{ }^{\circ}\text{C}$ for 0.4 h) and on a commercial LiFePO₄ powder for comparison (not reported here). The high resolution C1s spectrum of the uncoated foam (Fig. 3a – untreated) shows the carbon peak at 284.6 eV and is asymmetric in nature, while the O1s spectrum (Fig. 3b – untreated) shows a maximum at 532.6 eV indicating the presence of C–OH groups. This could indicate a partial oxidation of the foam surface which is a rather normal behavior of carbon

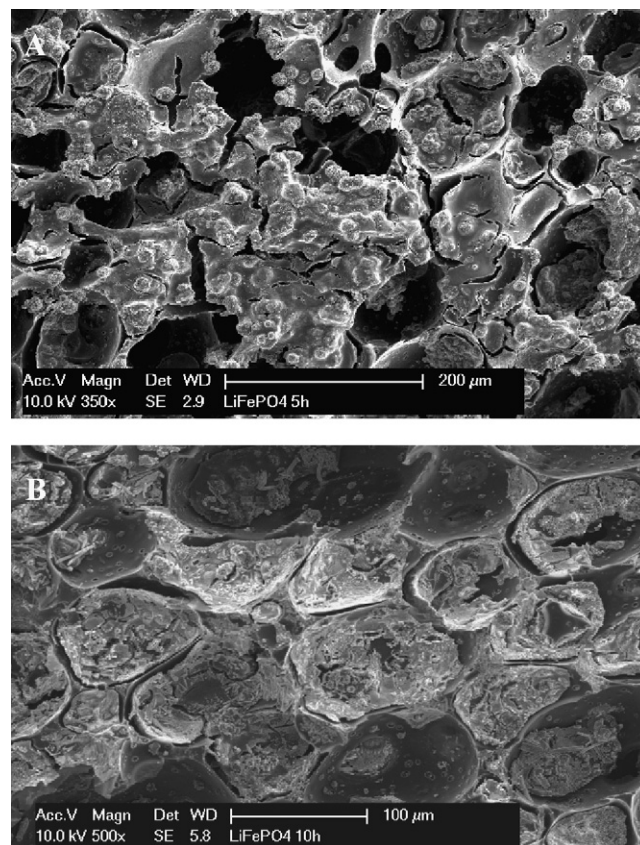


Fig. 2. HREM pictures of carbon foam–LiFePO₄ composites after annealing at $600\text{ }^{\circ}\text{C}$ for (a) 5 h and (b) 10 h, respectively.

nanostructures as previously reported [10]. The XPS survey spectra of the CF-LFP composites indicate that: (i) no XPS signals of Li, Fe and P have been detected; (ii) carbon and oxygen are the dominant species comprising the surface. In fact, the coated foams reveal a significant change in the XPS spectra of C1s and O1s compared to the uncoated. Considering the C1s profile, the main emission broadens with a significant shoulder towards higher binding energy consisting of several contributions and there is clearly enhanced emission of a feature near to 289 eV. The shoulder is consistent with an increased presence of hydroxyl groups, whereas the latter trend is consistent with an increase in relative amount of carboxyl functional groups [17]. The O1s spectra become more asymmetric and broader towards lower binding energy, consistent with an increase in the relative proportion of C=O and C–OH groups.

The presence of the C=O and C–OH groups on the surface of the LF-LFP composites can be explained by the partial oxidation of a carbon layer on the surface of the LiFePO₄ phase coated on the foam. The formation of the carbon layer resulted from the residue from citric acid used in the Pechini assisted sol–gel process as previously reported by Herstedt et al. [18] and confirmed by Rho et al. [19].

3.4. Electrochemical measurements

Electrochemical measurements have been performed on the composites prepared by soaking and annealed at $600\text{ }^{\circ}\text{C}$ under nitrogen for different times.

The CV curves indicate the potential range in which the lithium deintercalation/intercalation occurs and the phase transitions (if there is any) occur during this process.

The CV curves for the composites annealed at different times are shown in Fig. 4a–c. The corresponding deintercalation/intercalation potentials at the mean peak maxima as in

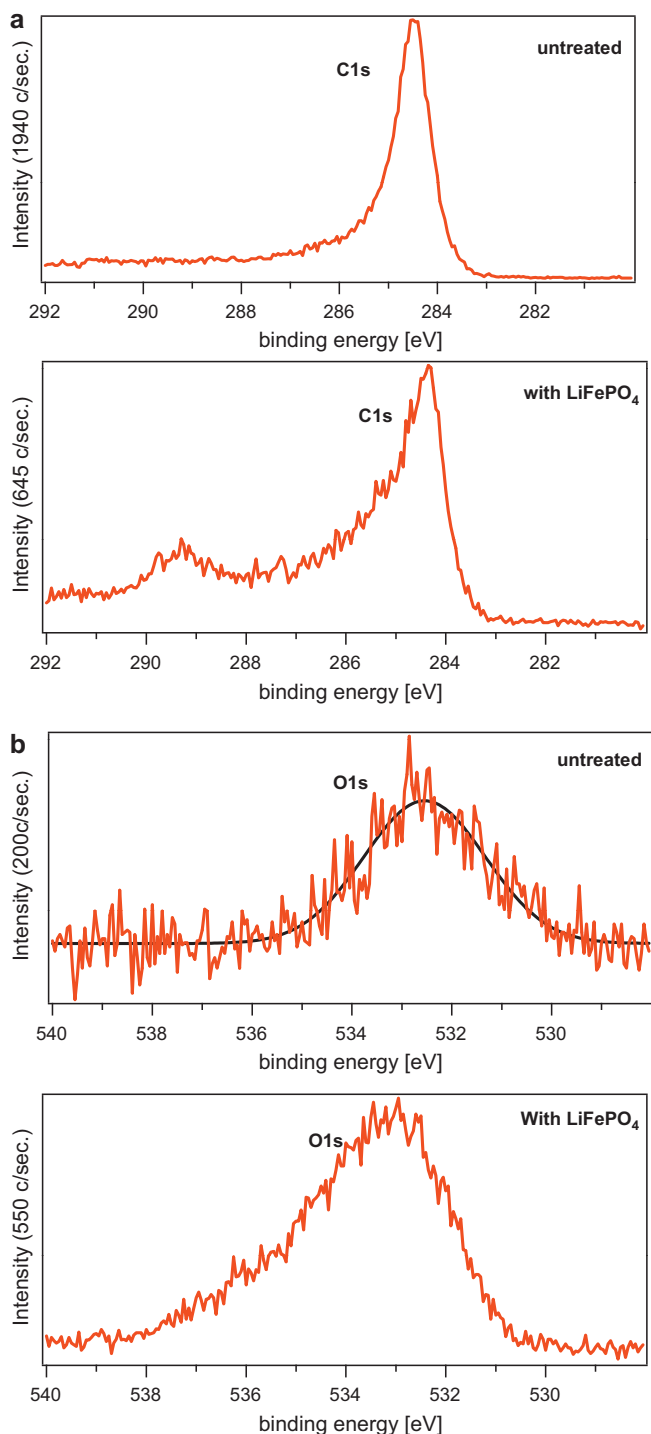


Fig. 3. XPS spectra (a) in the region of C1s for uncoated foams and LF-LFP composites; (b) in the region of O1s for uncoated foams and LF-LFP composites.

Fig. 4a–c are shown in Table 1. The measurements indicate clearly an improved kinetics of the lithium deintercalation/intercalation processes in the composites annealed at for shorter times ($t \leq 5$ h). After short annealing time ($t = 0.4$ h), the polarization in the first cycle is obvious and peak voltage separation is 0.30 V in the first cycle, while it is only 0.10 V from the second cycle (Fig. 4a). This is probably due to the fact that lithium diffusion and electrochemical kinetics reach an optimal state after the initial cycle. The very small difference between oxidation and reduction peak maxima could indicate a very small polarization occurring in the compos-

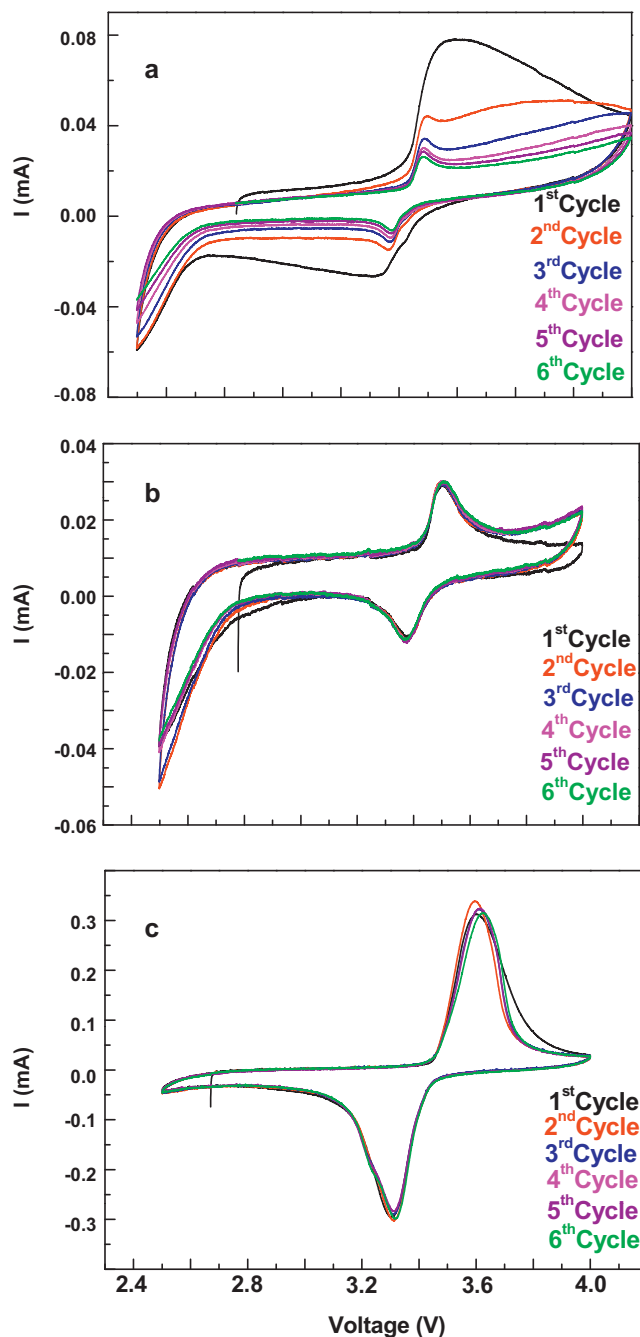


Fig. 4. Cyclic voltammograms recorded for the carbon foam–LiFePO₄ composites after annealing at $T = 600^\circ\text{C}$ for: (a) 0.4 h, (b) 5 h, and (c) 10 h, respectively (scan rate 0.05 mV s^{-1} , in the potential range 2.5–4.2 V vs. Li⁺/Li).

Table 1

Values of the deintercalation/intercalation potentials (peak maxima in Fig. 4a–c) for the carbon foam–LiFePO₄ composites after annealing under nitrogen at 600°C for different times.

Annealing time (h)	Cycle (nr)	Deintercalation potential (V)	Intercalation potential (V)
0.4	1	3.60	3.30
	2, 3, 4, 5, 6	3.50	3.40
5	1–6	3.50	3.37
	1–6	3.60	3.31

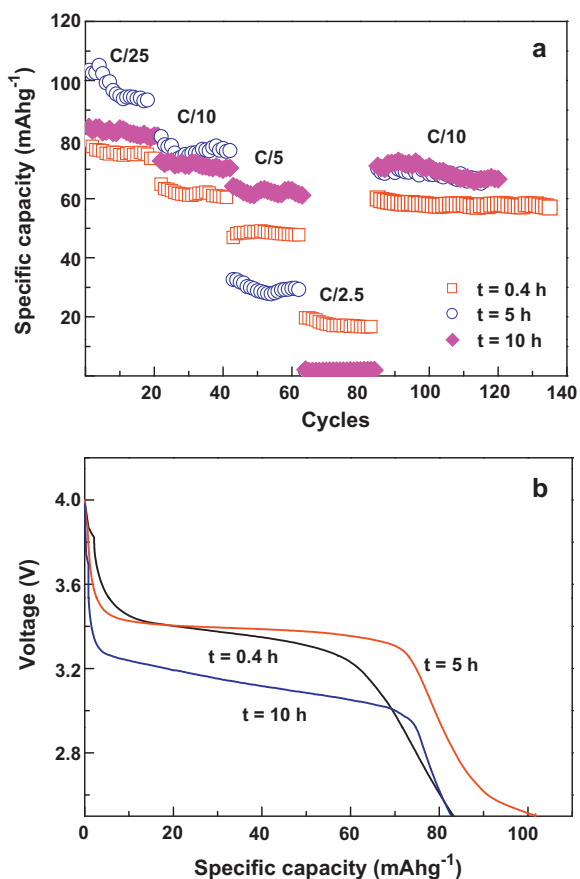


Fig. 5. (a) Discharge capacity and (b) discharge profile at C/25 discharge rate for carbon foam–LiFePO₄ composite samples that were annealed at $T=600\text{ }^{\circ}\text{C}$ for different times.

ites. At higher annealing times ($t=5\text{ h}$), a slight higher peak voltage separation was observed (0.13 V) during the charging and discharging cycles, whereas the first cycle showed a different shape only. This indicates clearly that the electrochemical kinetics was improved by the annealing. One of the possible explanations is the low polarization overpotential leading to higher Li-diffusion rates. This overpotential usually emerges from a combination of Li-diffusion rates and the intrinsic activation barrier of transferring electrons which could be high due to the small size of the particles that is to say to the high interparticle surface. By increasing the annealing time, the growth of the particles is expected that means a lower interparticle surface, consequently a lower energy barrier for the Li-diffusion in the composite. Moreover, the presence of a carbon layer on the LiFePO₄ as detected by the XPS analysis could improve the electronic conduction leading possibly to an improvement of the electrochemical processes. At higher annealing times ($t=10\text{ h}$, shown in Fig. 5c), despite a slight difference in the shape of the first cycle and a higher potential difference between oxidation and reduction (0.29 V), the peak maxima fall in a very narrow potential range confirming the “interaction” among the particle growth, the “cage effect” of the carbon framework and the carbon layer on the electrochemically active phase.

Each of the samples was prepared into electrodes and cycled at least 20 times at different C-rates ranging from C/25 to C/2.5. The higher loading is 40–45 wt.% LiFePO₄ on carbon, a value which is in agreement with the data in [14]. The discharge capacities for the carbon foam/LiFePO₄ composites are presented in Fig. 5a. The annealing time had a significant effect on the capacity of the battery. In fact, at lower discharge rates, higher specific capacities (for example 85 mAh g⁻¹ and 105 mAh g⁻¹ after 10 h and 5 h anneal-

ing times respectively at a discharge rate of C/25) were attained for longer annealing times. On the contrary, at higher discharge rate a lower capacity loss during the cycling was observed for samples annealed at shorter times (Fig. 5a, at C/2.5). This difference is likely due to the structural features of the composite materials as explained in the previous sections. The discharge profiles in Fig. 5b have noticeably curved profiles even at such a low discharge rate of C/25 for $t=0.4\text{ h}$ and $t=10\text{ h}$, respectively. The 3.4 V voltage drops as the cell discharges due to polarization. This is due to the diffusion resistance within the composite electrode [20]. On the other side, a less curved profile can be observed in the sample annealed for $t=5\text{ h}$ confirming the good quality of the sample.

Although the materials presented in this paper did not achieve the values of the specific capacities widely reported in the literature; the novel concept offers promising structural enhancements. The concept implies a continuous porous carbon network which featured macro-, meso- and nanopores to act as a conductive and very lightweight current collector to which the LiFePO₄ can be infiltrated in order to improve access into the porous architecture and increase the interface between the carbon and the active electrode material. The additional optimization of the annealing conditions can lead to further improvements of the electrochemical performances of the composites.

4. Conclusions

The influence of the annealing time under nitrogen atmosphere on lithium iron phosphate coated on commercial foams coated with olivine structured lithium iron phosphates as cathode materials has been successfully investigated. The composites have been prepared by soaking the foams in the starting solution, containing the ions. The composites were dried out, and finally thermally treated at $T=600\text{ }^{\circ}\text{C}$ for different times. The XRD analysis performed on powders prepared under similar conditions, indicated LiFePO₄ as major crystalline phase. The XPS analysis revealed the presence of the C=O and C–OH groups on the surface of the LF-LFP composites, which can be explained by the partial oxidation of a carbon layer on the surface of the LiFePO₄ phase coated on the foam. The formation of the carbon layer on the LiFePO₄ phase occurs particularly during the preparation of the Li-ion phosphates through the Pechini assisted sol-gel process.

The surface investigation on the prepared composites after annealing at $T=600\text{ }^{\circ}\text{C}$ for different times (ranging from 0.4 h and 10 h) showed a dependence of the morphology upon the annealing conditions. The composites showed a homogeneous coating of the olivine phase on the porous nanoarchitecture of the foams after soaking and annealing. During the annealing the growth of the LiFePO₄ crystalline phase on the other side and the “cage effect” of the sponge architecture opposing the growth can take place leading to the “deformation” of the thin walls inside the porous architecture of the foam.

The electrochemical properties of the powders as well as of the composites were found to be dependent upon the annealing conditions. After annealing for $t=5\text{ h}$ at the optimal annealing temperature (600 °C), the electrochemical measurements showed a good reproducibility of the peaks in the CV plots as well as narrower oxidation/reduction potential difference, which is representative of the good reversibility of the lithium extraction/insertion in the materials. The composites delivered a discharge capacity of 85 mAh g⁻¹ and 105 mAh g⁻¹ at a discharging rate of C/25 at room temperature for the samples annealed for 0.4 h and 5 h respectively. In the future, improvements to the electrochemistry may be achieved by optimizing the coating of lithium iron phosphate surrounding the carbon foam. This would increase the carbon–LiFePO₄ interface and potentially

improve the charge transfer kinetics. Further investigation into the application as e.g. supercapacitor electrode material may also be promising.

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Contributors: L. Dimesso coordinated all the synthesis and analytical work; performed the electrochemical characterizations. S. Jacke performed XPS-characterization on the foams and on the composites; useful discussion and suggestions; prepared and revised the manuscript. C. Spanheimer performed the synthesis of the powders and composites; useful technical discussion. W. Jaegermann, supervisor of the group; useful discussion.

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