Journal of Alloys and Compounds 516 (2012) 119–125

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Preparation and characterization of carbon foams–$LiCoPO_4$ composites

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ARTICLE INFO

Article history:
Received 21 September 2011
Received in revised form
16 November 2011
Accepted 29 November 2011
Available online 13 December 2011

Keywords:
Battery
Lithium cobalt phosphate
Sol–gel process
Composites
Nitrogen
Air

ABSTRACT

The preparation and characterization of composites consisting of carbon foams coated with olivine structured lithium cobalt phosphate is reported. The composites are prepared by a Pechini assisted sol–gel process and treated under different conditions in flowing nitrogen and in flowing air. The structural, morphological and electrochemical properties were found to be dependent upon the annealing conditions as time and atmosphere. After annealing in nitrogen, the formation of the $LiCoPO_4$ phase on the foams is observed at $T = 730\,^{\circ}C$. The photoelectron emission spectra reveal divalent cobalt ions in the composites. The $LiCoPO_4$/foam composites deliver a discharge specific capacity of 100 mAh g^{-1}, at a discharge rate of C/25 and room temperature. After a pre-annealing in air then the annealing in nitrogen, the voltammetric curves show values of the reduction/oxidation processes at 4.6 V and 5.2 V respectively. The electrochemical measurements revealed a decrease of the capacity fade (~26% at C/10, RT). A plateau in the specific capacity as a function of the potential has been observed.

1. Introduction

With the increasing demand for electric and hybrid electric vehicles to resolve energy and environmental problems, cathode materials with high specific energy density, high power density and excellent thermal stability are necessary for Li-ion batteries (LIBs) [1]. The creation of redox-active transition metal framework structures that host mobile interstitial Li-ions is crucial in developing high capacity LIBs. Lithium transition metal phosphates such as $LiFePO_4$ [2], $LiMnPO_4$ [3], $Li_3V_2(PO4)_3$ [4,5] and $LiVPO_4F$ [6,7] have been recognized as promising positive electrodes for these systems because of their energy storage capacity combined with electrochemical and thermal stability.

Among the $LiMPO_4$ (M = Fe, Mn, Ni and Co) systems, Okada et al. [8] have shown that $LiCoPO_4$ has the highest redox potential. $LiCoPO_4$ is the only example of this class of materials that is suitable for 5 V performances. In fact it can be considered as one of the best examples of 5 V cathode materials because of its high specific capacity and voltage. However, studies on $LiCoPO_4$ are scarce because the existing preferred nonaqueous electrolytes are found to be unstable in the high-voltage range (≥4.8 V) where cobalt reduction/oxidation reactions can occur. Efforts toward improving nonaqueous electrolytes have made $LiCoPO_4$ an attractive cathode to explore in the high charge voltage regime, up to 5 V. Although the reversibility of lithium extraction-insertion from/into $LiCoPO_4$ was demonstrated in a few reports [9–12], a severe capacity fading during cycling has limited the use of this material in practical applications. As result, less attention has been paid toward the development of $LiCoPO_4$ cathode in lithium batteries using nonaqueous electrolytes.

$LiCoPO_4$ can be prepared by using solid state reactions [10–12] and soft chemistry routes [13–17]. The wet-chemistry technique offering improvement in the terms of material preparation has been extensively used as a low-temperature synthesis route ($T < 200\,^{\circ}C$). Improvements in the battery performance can be achieved by reconfiguring the electrode materials currently employed in 2-D batteries into 3-D architectures. The use of commercially available carbon foams as framework for cathode materials offers several advantages such as good inter-particle conductivity, an efficient transport route for the solvated ions and hence possibly superior battery performances, a greater infiltration of the electrolyte into the battery leading to a better electrical contact, a variety of configurations depending on the particular applications. These advantages can be used for manufacturing lithium ion batteries. Recently, Dimesso et al. [18,19] have reported the preparation of $LiFePO_4$–carbon foams composites by using a Pechini assisted sol–gel process. The authors, by investigating the electrochemical performances of the composites as function of the annealing temperature and time, obtained a specific capacity of 80 mAh g^{-1} at a discharging rate of C/10 measured at room temperature after annealing at $T = 600\,^{\circ}C$ for $t = 5$ h [19]. The annealing treatment is

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doi:10.1016/j.jallcom.2011.11.147

still an important and necessary step in the preparation of Li-ion phosphates. In the Fe-containing lithium phosphates, it is performed to avoid secondary reactions but mainly the Fe^{2+}/Fe^{3+} reaction which would compromise seriously the efficiency of the product in the cathode material. In the Co-containing system the influence of the annealing atmosphere has not been fully cleared. Dimesso et al. [20] investigated the influence of the annealing atmosphere on the structure, morphology and electrochemical performances of the $LiCoPO_4$ system. The authors observed a quick fade in capacity (≥50%) after annealing in air independently of the annealing time. From the experimental data, the authors supposed that the absence of electron-conducting phases (e.g.: the residual carbon from the sol–gel process) and the possible lack of lithium ions due to the treatment at high temperature could reasonably lead to a faster formation of the $CoPO_4$ phase during the delithiation process. $CoPO_4$ is unstable at room temperature, and sufficient quantities of this material, which often becomes non-crystalline, could cause the fade in the capacity. On the other side, a lower capacity fade (∼35%) was measured on the $LiCoPO_4$ phase after annealing under nitrogen. The lower capacity fading was explained by the presence of elemental carbon into the material as well as by the cobalt–phosphide phase on the surface of the particles which work as "shield" against (or slow down) the amorphization of the $CoPO_4$.

Following the previous results we report the synthesis and the characterization of carbon foams–$LiCoPO_4$ composites (hereafter CF-LCP), prepared by the Pechini-assisted sol–gel method, using water as solvent, and thermally treated under different conditions of atmosphere and temperature. The electrochemical performances have been discussed in relation to the structural and to the morphological investigation carried out on the composites.

2. Experimental

The experimental procedures for the preparation and characterizations of the samples are similar to those reported earlier [20]. The samples are prepared by dissolving in water $Li(CH_3COO){\cdot}2H_2O$ (lithium acetate), $Co(CH_3COO)_2{\cdot}4H_2O$ (cobalt(II) acetate) as precursors (molar ratio 1:1) with citric acid (2 × mol [Co]), then phosphoric acid in equimolar ratio with Li and Co ions was added. Pure water, due to the rheological properties, favored the infiltration of the ions containing solution into the porous architecture of the foams. The commercial foams (GRAFOAM® carbon foams, a registered trade name from GRAFTECH International Ltd. [21]) 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 80 °C for 2 h. After rinsing with distillate water the samples have been annealed under different conditions. According to previous results, a first set of CF-LCP composites have been annealed at T = 730 °C for different times (t) ranging between 5 and 18 h under a nitrogen atmosphere. A second set of composites have been annealed in air at T = 300 °C for t = 0.5–12 h then under nitrogen for t = 12 h at T = 730 °C.

The structural analysis of the samples was performed by X-ray powder diffraction using a D8 Bruker powder diffractometer (Cu Kα_1 + Cu Kα_2 radiation) with a theta/2 theta Bragg–Bentano 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 a monocromated Al Kα (1468.6 eV) source. Electrochemical studies (e.g.: cyclic voltammetry (CV)) have been carried out with a multichannel potenstiostatic–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. To measure the composites, the foam disks were direct assembled into the cell and a few drops of the electrolyte were added. In the cell, Li metal was used as anode, SelectiLyte LF30 (1 M Li-FAP in ethylene-carbonate: di-methyl-carbonate 1:1 (wt/wt), Merck KGaA, Germany) as electrolyte [22,23], Celgard®2500 as separator. All electrical measurements have been performed at room temperature.

3. Results and discussion

3.1. Structural analysis

A detailed structural investigation of the $LiCoPO_4$ phase as function of the annealing conditions has been previously reported [20].

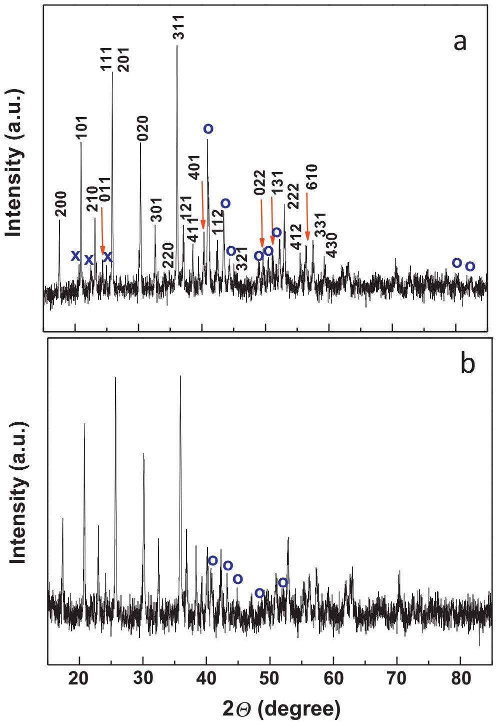

Fig. 1. X-ray diffraction patterns of the prepared $LiCoPO_4$ powders annealed (a) under nitrogen at T = 730 °C for t = 12 h, (b) in air at T = 300 °C for t = 12 h then in nitrogen at T = 730 °C for t = 12 h. Secondary phases are indicated as (**x**) for $Li_4P_2O_7$ and as (**o**) for Co2P.

The XRD-diffractograms of the $LiCoPO_4$ prepared and treated under very similar conditions of the composites are shown in Fig. 1a and b. All the diffraction peaks have been indexed with the olivine-type symmetry which confirms that the structure of the prepared powders corresponds to the orthorhombic $LiCoPO_4$. By annealing under nitrogen at temperatures ranging between 300 °C and 730 °C (for t = 5 h), the presence of $LiCoPO_4$ as single crystalline phase has been detected. For longer annealing time ($t \geq 12$ h), the XRD spectra showed the presence of crystalline reflections attributed to $Li_4P_2O_7$ and to Co2P as secondary phases (indicated with (x) and with (o) respectively in Fig. 1a [20,24].

After annealing in air at T = 300 °C for t = 12 h then in nitrogen at T = 730 °C for t = 12 h, the XRD spectra revealed the presence of $LiCoPO_4$ as major crystalline and reflections due to Co2P as secondary phase (Fig. 1b). The formation of such secondary phases, particularly of Co2P, occurs due to the reduction at the grain boundaries of the $LiCoPO_4$ crystalline phase by heat treatment at high temperatures (≥700 °C) under inert atmosphere. Whether the presence of these secondary phases leads to an improvement of the electrochemical performance of $LiCoPO_4$ is still under debate.

3.2. HREM

In the commercial foams, the authors observed the presence of numerous apertures, suggesting that the interior pore system is interlaced and the nanoporous architecture is uniform [18]. 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 [25]. The authors emphasize that in this "sponge" approach, the electrolyte layer is formed around a random 3-D network of electrode material. Short transport-path characteristics between the insertion electrodes are preserved with this arrangement.

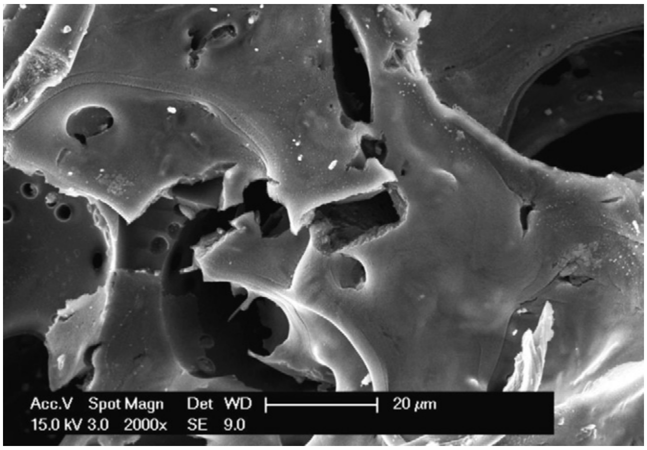

Fig. 2. Micrograph of a carbon foam–$LiCoPO_4$ composite after annealing at $T = 730\,^{\circ}C$ for $t = 5$ h in nitrogen atmosphere.

A typical micrograph of the CF-LCP composite prepared by soaking and annealed at 730 °C for $t = 5$ h is shown in Fig. 2. By soaking, the foam surface is supposed to be covered by a continuous layer of liquid in which the Li^+, Co^{2+} and $(PO_4)^{3-}$ ions are uniformly distributed. The slow evaporation of the solvent should lead to a “uniform” layer on the foam surface. However other factors, such as the viscosity of the solution, seem to influence the morphology of the $LiCoPO_4$ layers on the carbon foams surface. Unlike the Fe-containing solutions, the Co-containing solutions tend to turn to gel much faster under similar conditions of temperature and pressure giving rise to the $LiCoPO_4$ phase deposited on the surface of the foam.

A different morphological behavior has been detected after the pre-annealing in air then in nitrogen as shown in Fig. 3a and b. The morphological investigation of the CF-LCP composites shows the $LiCoPO_4$ material filling the apertures on the surface of the foam (Fig. 3a). The presence of cracks and voids in the structure of the layer are clearly visible (Fig. 3b). Such a presence could be explained supposing a multidirectional growth of the $LiCoPO_4$ crystalline phase occurring during the annealing, the “gas evolution” coming from the formation of water, CO and CO_2 as by-products of the oxidation reaction of the acetates and of the citrates as widely reported in the literature. The mechanical stress arising from these two effects could cause the cracks, the voids and bring to the “deformation” of the thin walls inside the porous architecture of the foams with partial or total break-downs of the $LiCoPO_4$ crystalline phase from the foam walls.

3.3. XPS analysis

The results of the XPS analysis carried on uncoated foams have been previously reported [19]. The XPS data indicated the presence of C—OH groups, possibly due to a partial oxidation of the foam surface which is a rather normal behavior of carbon nanostructures [26]. The XPS survey spectra of the CF-LCP composites detected the presence of carbon, cobalt, oxygen, phosphorus and lithium, and revealed no impurities on the surface of the composites. The photoelectron emission spectra of C1s, Co2p and P2p are shown in Fig. 4a–c. The asymmetry of the C1s photoelectron line (Fig. 4a) toward higher binding energy is due some amount of carboxyl functional groups (including C—O and/or C═O) on the surface [26]. The $Co2p_{3/2}$ photoelectron emission at binding energy of 783 eV and the energy position of the satellites S at ~7 eV from the main peak of $Co2p_{3/2}$ indicate divalent cobalt ions in the CF-LCP composites (Fig. 4b). In the P2p photoelectron spectrum, the peak maximum was observed 134.5 eV binding energy, that indicates the valence state for P element in the composite 5+ as recently reported by Tan et al. [27] (Fig. 4c).

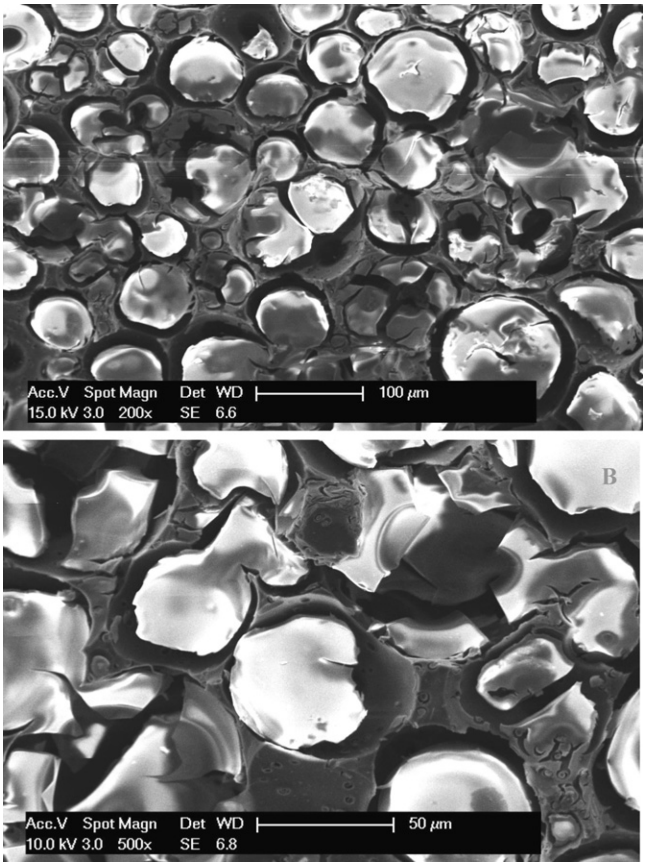

Fig. 3. HREM pictures of carbon foam–$LiCoPO_4$ composites after annealing in air at $T = 300\,^{\circ}C$ for $t = 5$ h then in nitrogen at $T = 730\,^{\circ}C$ for $t = 12$ h.

3.4. Electrochemical measurements

A typical cyclic voltammogram (CV) for $LiCoPO_4$/carbon foams, annealed at $T = 300\,^{\circ}C$ in air for $t = 12$ h, then at $T = 730\,^{\circ}C$ for $t = 12$ h in nitrogen, using Li metal as counter and reference electrode cycled in the range 3.0–5.3 V is shown in Fig. 5. The CV curves show that the shape of the first cycle is slight different while CV-profiles are reduplicated from the second cycle as revealed by the very close values of the mean peak maxima in the cathodic region at 4.60 V. The mean peak maximum in the oxidation region of the first cycle lies at 5.20 V, while the mean peak maxima shift from 5.10 V to 5.20 V from the second cycle on. This result is in good agreement with previous cyclic voltammetry investigations on $LiCoPO_4$ [8,10,27,28]. The shoulder at about 4.88 V in the oxidation curve could indicate a two-steps mechanism of lithium deintercalation as previously reported [26].

A very similar electrochemical behavior has been observed in the CV-curves of the CF-LCP composites, annealed under nitrogen at $T = 700\,^{\circ}C$ for $t = 12$ h where the mean peak maxima in the cathodic region were 4.5 V.

The difference in the shape of the first cycle of the voltammetric curves can depend upon several parameters such as structural and morphological changes of the cathode and anode materials, chemical reactions occurring within the electrolyte, at the electrolyte–anode and electrolyte–cathode interfaces. The influence of these parameters has been investigated in several systems as $LiCoO_2$, $LiMnO_4$ and $LiFePO_4$ and the results have been reported

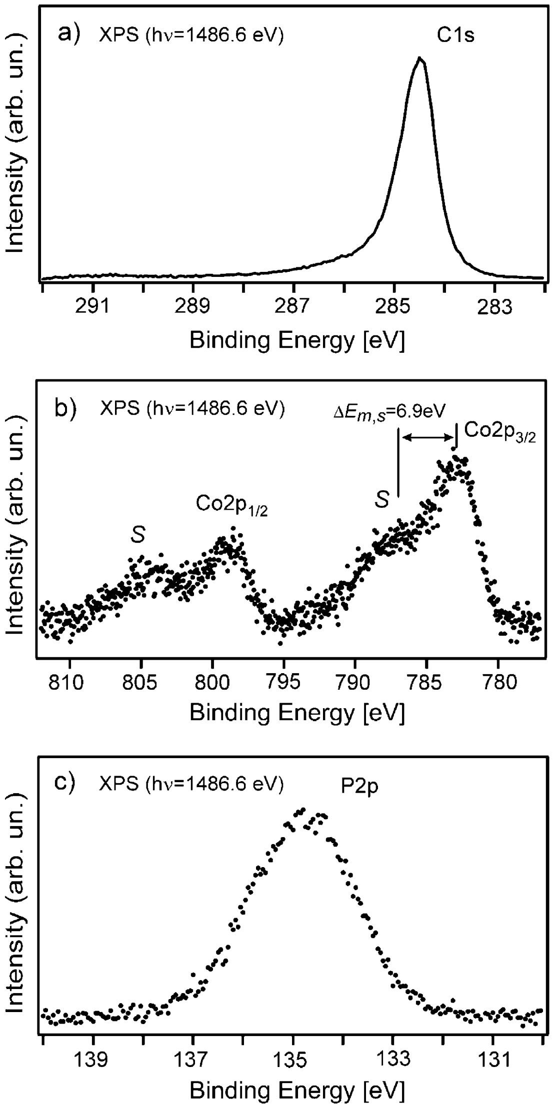

Fig. 4. (a) C1s, (b) Co2p and (c) P2p photoelectron emission spectra of the as prepared $LiCoPO_4$/C composites annealed in air at $T = 300\,°C$ for $t = 12$ h then in nitrogen at $T = 730\,°C$ for $t = 12$ h.

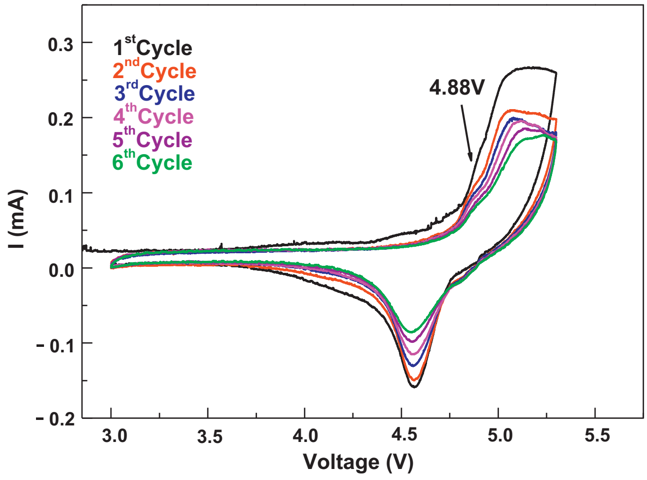

Fig. 5. Cyclic voltammograms recorded for the carbon foams/$LiCoPO_4$ composites after annealing in air at $T = 300\,°C$ for $t = 12$ h, then in nitrogen at $T = 730\,°C$ for $t = 12$ h (scan rate 0.05 mV s^{-1}, in the potential range 3.0–5.3 V vs. Li^+/Li).

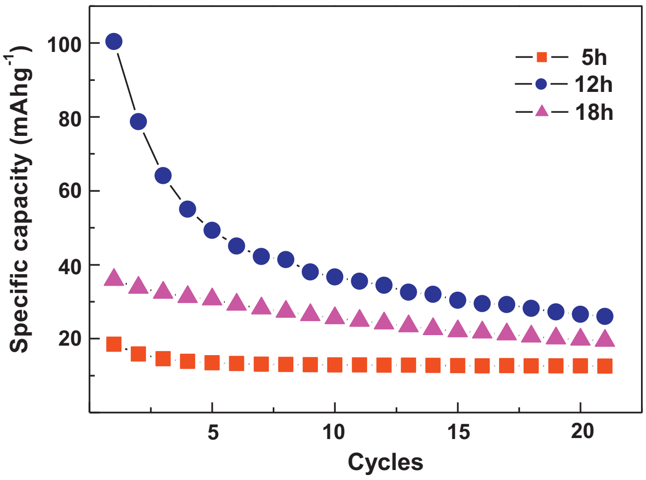

Fig. 6. Discharge capacity measured at a charge rate of C/25 and room temperature, for carbon foam/$LiCoPO_4$ composites annealed in nitrogen at $T = 730\,°C$ for different times.

elsewhere [29–31]. However, we have found no data concerning the $LiCoPO_4$ system. We can reasonably assume that the marked capacity fade observed after the first cycle can be due to surface reactions involving the change of the structure of LCP from olivine to an amorphous phase, as observed in the $LiFePO_4$ system [31 and references herein]; the formation of a passive, solid-electrolyte interface (SEI) layer on the surface of both the cathode and the anode materials.

The CF-LCP composites were cycled at different C-rates ranging from C/25 to C/2. The higher loading is 35–40 wt% $LiCoPO_4$ on carbon, a value which is in agreement with the data previously reported [18,32]. The discharge capacity (measured at C/25 discharge rate and at room temperature) for composites annealed at $T = 730\,°C$ for different times is shown in Fig. 6. The annealing time had a significant effect on the capacity of the composite. At the beginning, the specific capacity increased by increasing the annealing time reaching a maximum of 100 mAh g^{-1} at a discharge rate of C/25 after $t = 12$ h. At longer annealing times ($t = 18$ h) a decrease of the specific capacity has been observed. At higher discharge rates, the specific capacity of the $LiCoPO_4$ decreases dramatically reaching barely 5 mAh g^{-1} at a discharge rate of C/2.

The electrochemical activity of the $LiCoPO_4$ system is still a controversial debate and has not been fully understood. Extensive investigations on the electrochemical properties of the Li_xCoPO_4 system, prepared by sol–gel process, claim that a two-step delithiation process occurs and that it is an intrinsic property of the system [33]. Furthermore, the in situ and ex situ XRD investigations showed that the crystalline phase was only a lithium-poor phase; no "$CoPO_4$" was identified even though $LiCoPO_4$ was fully charged [34]. The galvanostatic (C/25) charge-discharge of the cell with CF-LCP composites annealed under nitrogen as cathode reveals a high capacity lost in the first cycle, which is consistent with previous data reported for this compound (see Fig. 7a and b) [34 and references therein]. After being charged to the composition "$CoPO_4$", the cell delivers about 60% of the theoretical capacity (167 mAh g^{-1}). The lithium extraction–insertion in $LiCoPO_4$ was demonstrated to proceed in a reversible manner. Amine et al. [10] reported that the diffraction pattern of the material after one complete cycle is very similar to the one of the pristine compound. This result would indicate that the capacity loss in the first cycle cannot be attributed to the irreversible phase transitions occurring upon cycling. The limited electronic/ionic transport, well-known for olivine-type metallophosphates, can contribute to the loss in capacity and according to Bramnik et al. [35] the discharge capacity

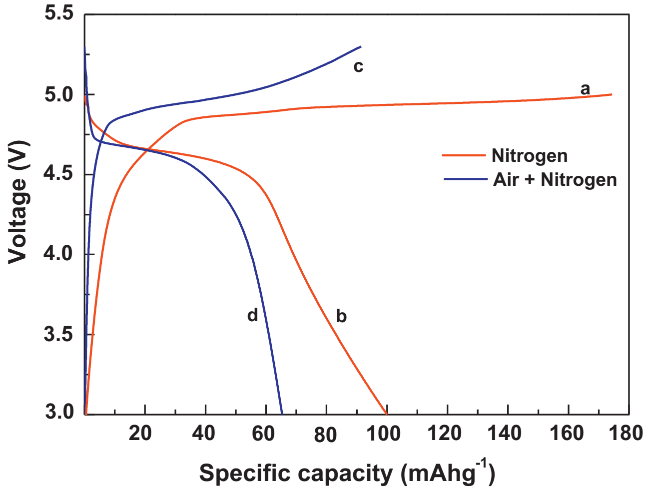

Fig. 7. Voltage profiles during the first galvanostatic (C/25, RT, 5.0 V) (a) charge, (b) discharge cycle of the carbon foam–$LiCoPO_4$ composites annealed in nitrogen at $T = 730\,^{\circ}C$ for $t = 12$ h; (c) charge, (d) discharge cycle of carbon foam–$LiCoPO_4$ composites (C/25, RT, 5.3 V) annealed in air at $T = 300$ for $t = 12$ h, then in nitrogen at $T = 730\,^{\circ}C$ for $t = 12$ h.

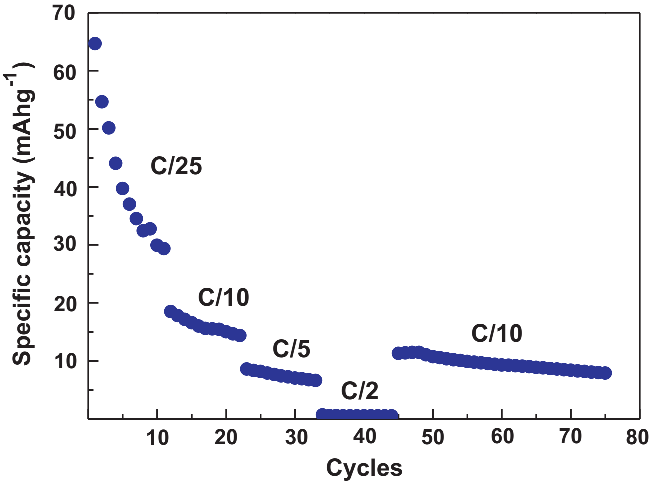

Fig. 8. Discharge capacity measured at different charge rates and room temperature, for carbon foam/$LiCoPO_4$ composites annealed in air at $T = 300$ for $t = 12$ h, then in nitrogen at $T = 730\,^{\circ}C$ for $t = 12$ h.

should increase at low currents rates. However, the same authors reported that upon galvanostatic cycling at low current density (lower than C/6), the electrochemical performance of the $LiCoPO_4$ phase deteriorates. This behavior was explained by the contribution of the electrolyte decomposition, which is more significant at slow charging of the cell. In fact, the degradation of the electrolyte on the cathode side may cause a limitation in mass transport on the cathode/electrolyte interface. Our experimental results and experience are in partial agreement only with this explanation. In fact, after annealing under nitrogen the charge capacity in the first cycle is higher than the theoretical capacity of $LiCoPO_4$ (Fig. 7a) which could be explained by the electrolyte decomposition, as also reported by Tan et al. [27 and references herein]. This decomposition could lead to an irreversible charge/discharge process. On the other hand, in our experiments we measured this charge capacity galvanostatic C/25 and found out that it is ca. 5% higher only than the theoretical capacity of the Co-containing system (measured at 5.0 V). This fact can be explained by the higher chemical stability of the electrolyte, used in our experiments, in the 5 V range than the conventional $LiPF_6$ [23]. The higher stability indicated us that its influence on the capacity fade of the $LiCoPO_4$ system can be considered minimal. An additional factor to be considered can be the growth of secondary phases (particularly Co2P as confirmed by the XRD analysis) on the grain boundaries that could behave like "resistors" allowing the electron flow but adding a further potential on the surface that would inhibit the Li-ions transfer. This additional surface potential may be the reason of the degradation of the electrochemical performance of the system with the time [20].

A different electrochemical behavior is shown by the CF-LCP composites after annealing in air at $T = 300\,^{\circ}C$ then in nitrogen at $T = 730\,^{\circ}C$ for $t = 12$ h as shown in Fig. 8. At the end of the first cycle at a discharge rate of C/25, the specific capacity is 65 mAh g^{-1} (Fig. 7d) while this value decreases to 30 mAh g^{-1} after the 10th cycle. At higher discharge rates, the specific capacity of the CF-LCP composites decreases reaching 10 mAh g^{-1} at a discharge rate of C/5 and a decrease of the capacity fade was observed as well as reported in Table 1. Furthermore, a discharge plateau appears at around 4.6 V for the LFC-CF composites pre-annealed in air (Fig. 7d). This value is consistent with the foregoing cyclic voltammetric data which show reduction maxima peaks at around 4.6 V. In our case the annealing in air at lower temperature could optimize the stoichiometry of the $LiCoPO_4$ phase, leading to a decrease of the capacity fade to 26% at a discharge rate of C/10. Although the lower capacity fade the CF-LCP composites pre-annealed in air delivered a lower specific capacity than those annealed under nitrogen only. This behavior can be partially explained with the decomposition of the electrolyte that could occur above 5.0 V as confirmed by the profile of the charge capacity in the first cycle (Fig. 7c). In fact, a sudden change of the slope in the charge curve can be clearly observed. This change could be related to the irreversible degradation of the electrolyte with the formation of secondary products which inhibit the kinetic of the deintercalation/intercalation processes of the Li-ions. This behavior can be better explained by the lower amount (or lack) of carbon and consequently of Co2P in the samples pre-annealed in air. The content of the carbon has been determined by the elemental analysis (CHN-X) on $LiCoPO_4$ powders prepared by the Pechini-assisted sol–gel process under very similar conditions as the composites and annealed under different conditions

Table 1
Summary of the values of the capacity fade (in %, referred to the 1st–10th cycles) of the $LiCoPO_4$/carbon composites, annealed under different conditions, measured at different discharge rates.

Sample	Air		Nitrogen		Discharge rate (C)	Specific capacity (mAh g^{-1})[a]	Capacity fade (%)
	T (°C)	t (h)	T (°C)	t (h)			
LCP-CF-N	–	–	730	12	C/25	100	63.5
LCP-CF-A-N	300	12	730	12	C/25	65	53.8
					C/10	19	26.3
					C/5	9	22.2
					C/2	Too low	–
					C/10-ret	11	9.1

[a] Measured at the first cycle.

Table 2
Content of the residual amorphous carbon (wt%) of $LiCoPO_4$ powders annealed under different conditions (the measured values are an average of repeat determination).

Sample	Air		Nitrogen		C (wt%)
	T (°C)	t (h)	T (°C)	t (h)	
LCP-CF-N	–	–	730	12	9.5
LCP-CF-A	300	0.5	–	–	8.6
LCP-CF-A	300	0.5	730	12	5.5

of atmosphere and temperature. The results of the CHN-X investigation are summarized in Table 2. The content of the carbon after annealing in nitrogen is higher than that one after the pre-annealing in air. The higher amount of the carbon into the $LiCoPO_4$ phase has led to the formation of a higher amount of Co2P (as confirmed by the XRD analysis as in Fig. 1a and b) resulting in a higher electrical conductivity and consequently in a higher discharge capacity. Very similar experimental results have been reported by Wolfenstine et al. [36 and references herein] who investigated the influence of different atmospheres on the electrochemical performances of $LiCoPO_4$ phase prepared by a solid state reaction. The authors concluded that heating under inert atmosphere (argon in their case) does not provide sufficient enough electrical conductivity and a small enough particle size required to achieve a high discharge capacity for $LiCoPO_4$ to be used as cathode in Li-ion batteries. In our case, a higher first cycle discharge capacity has been observed in the carbon foam–$LiCoPO_4$ composites prepared by a Pechini-assisted sol–gel process compared to the $LiCoPO_4$ powders prepared under very similar conditions. Additional procedures such as adding a conducting coating and/or lattice doping are needed in order to reduce the capacity fade of the $LiCoPO_4$ phase.

4. Conclusions

In this work, the synthesis and the characterization of carbon foams–$LiCoPO_4$ composites, prepared by the Pechini-assisted sol–gel method, using water as solvent is reported. The composites were prepared by soaking the carbon foams in aqueous solutions, containing the starting ions. After drying out, the composites were thermally treated under different conditions.

After annealing in nitrogen at $T = 730^{\circ}$C for $t = 12$ h, the XRD analysis performed on powders prepared under similar conditions, indicated $LiCoPO_4$ as major crystalline phase, $Li_4P_2O_7$ and to Co2P as secondary phases. The morphological investigation showed a uniform distribution of the $LiCoPO_4$ phase on the surface of the foam. The discharge capacity of the first cycle (galvanostatically measured (C/25) at room temperature) of the $LiCoPO_4$/C foams composite reached 100 mAh g^{-1}.

The XRD spectra of the composites annealed in air at $T = 300\,^{\circ}$C for $t = 12$ h then in nitrogen at $T = 730^{\circ}$C for $t = 12$ h, detected $LiCoPO_4$ as major crystalline phase and a smaller amount of Co2P as secondary phase. The morphological investigation revealed the filling of the pores on the surface of the foam. The presence of cracks and voids in the structure of the layer could be explained supposing the multidirectional growth of the $LiCoPO_4$ crystalline phase occurring during the annealing, and/or the “gas evolution” coming from the formation of water, CO and CO_2 as by-products of the oxidation reaction of the acetates and of the citrates. The mechanical stress arising from these two effects could cause the cracks, the voids and bring to the “deformation” of the thin walls inside the porous architecture of the foams with partial or total break-downs of the $LiCoPO_4$ crystalline phase from the foam walls. The CV curves show that the shape of the first cycle is slight different while CV-profiles are reduplicated from the second cycle on. The values of the reduction/oxidation processes were 4.6 V and 5.2 V respectively. The specific capacity of the $LiCoPO_4$/C foams composites, measured at a discharge rate of C/25, RT, was 65 mAh g^{-1}.

The enhanced discharge capacity of the $LiCoPO_4$/C-foams composites annealed under nitrogen compared to the in air pre-annealed samples was a result of its higher electrical conductivity due to the presence of cobalt phosphides and increased carbon content into the $LiCoPO_4$ phase.

Role of funding source

The authors thank the *Deutsche Forschungsgemeinschaft* (DFG) (Project: *Sonderforschungsinitiative Projekt PAK-177*) for the financial support during this work. The DFG promote and support financially the publication of the scientific results obtained during the projects. The DFG had no involvement in study design; in the collection, analysis and interpretation of data; in the writing of the report, and in the decision to submit the paper for publication.

Acknowledgment

Many thanks are owed to Mr. J.-C. Jaud for the technical assistance in the XRD analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2011.11.147.

References

[1] D.W. Han, Y.M. Kang, R.Z. Yin, M.S. Song, H.S. Kwon, Electrochem. Commun. 11 (2009) 137–140.
[2] A.K. Padhi, K.S. Nanjundaswami, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188.
[3] G. Li, H. Azuma, M. Tohda, Electrochem. Solid-State Lett. 5 (2002) A135.
[4] H. Huang, S.C. Yin, T. Kerr, L.F. Nazar, Adv. Mater. 14 (2002) 1525.
[5] S.C. Yin, P. Strobel, M. Anne, L.F. Nazar, J. Am. Chem. Soc. 125 (2003) 10402.
[6] J. Barker, M.Y. Saidi, J.L. Swoyer, Method of making lithium metal compounds useful as cathode active materials, WO Patent WO 02/44084 A2 (2002).
[7] J. Barker, M.Y. Saidi, J.L. Swoyer, Electrochem. Solid-State Lett. 6 (2003) A1.
[8] S. Okada, S. Sawa, M. Egashira, J. Yamaki, M. Tabuchi, H. Kageyama, T. Konishi, A. Yoshino, J. Power Sources 97–98 (2001) 430.
[9] M. Nakayama, S. Goto, Y. Uchimoto, M. Wakihara, Y. Kitajima, Chem. Mater. 16 (2004) 3399.
[10] K. Amine, H. Yasuda, Y. Yamachi, Electrochem. Solid-State Lett. 3 (2000) 178–179.
[11] J.M. Lloris, C. Pèrez Vicente, J.L. Tirado, Electrochem. Solid-State Lett. 5 (2002) A234.
[12] B. Jin, H.B. Gu, K.W. Kim, J. Solid State Electrochem. 12 (2008) 105–111.
[13] N.N. Bramnik, K. Nikolowski, D.M. Trots, H. Ehrenberg, Electrochem. Solid-State Lett. 11 (6) (2008) A89–A93.
[14] Gangulibabu, D. Bhuvaneswari, N. Kalaiselvi, N. Jayaprakash, P. Periasamy, J. Sol–Gel Sci. Technol. 49 (2009) 137–144.
[15] M.S. Bhuwaneswari, L.L. Dimesso, W. Jaegermann, J. Sol–Gel Sci. Technol. 56 (2010) 320–326.
[16] R. Vasanthi, D. Kalpana, N.G. Renganathan, J. Solid-State Electrochem. 12 (2008) 961.
[17] C. Julien, Ionics 6 (2000) 30.
[18] L. Dimesso, C. Spanheimer, S. Jacke, W. Jaegermann, J. Power Sources 196 (2011) 6729.
[19] L. Dimesso, S. Jacke, C. Spanheimer, W. Jaegermann, J. Alloys Compd. 509 (2011) 3777–3782.
[20] L. Dimesso, S. Jacke, C. Spanheimer, W. Jaegermann, Investigation on $LiCoPO_4$ powders as cathode materials annealed under different atmospheres, J. Solid State Electrochem., doi:10.1007/s10008-011-1441-5, in press.
[21] http://www.graftec.com/PRODUCTS/Carbon-Foams.aspx.
[22] M. Schmidt, U. Heider, K. Kuehner, R. Oesten, M. Jungnitz, N. Ignatev, P. Sartor, J. Power Sources 97–98 (2001) 557.
[23] J.S. Gnanaraj, E. Zinigrad, M.D. Levi, D. Aurbach, M. Schmidt, J. Power Sources 119–121 (2003) 799–804.
[24] B. Ellis, P. Herle Subramanya, Y.H. Rho, L.F. Nazar, R. Dunlap, L.K. Perry, D.H. Ryan, Faraday Discuss. 134 (2007) 119–141.
[25] J.W. Long, B. Dunn, D.R. Rolison, H.S. White, Chem. Rev. 104 (2004) 4463–4492.
[26] M.S. Bhuwaneswari, N.N. Bramnik, D. Ensling, H. Ehrenberg, W. Jaegermann, J. Power Sources 180 (2008) 553.
[27] S.F. Waseem, S.D. Gardner, G. He, W. Jiang, U. Pittmann Jr, J. Mater. Sci. 133 (1998) 3151–3162.

[28] L. Tan, Z. Luo, H. Liu, Y. Yu, J. Alloys Compd. 502 (2010) 407–410.
[29] J. Wolfenstine, J. Allen, J. Power Sources 136 (2004) 150.
[30] D. Zhang, B.S. Haran, A. Durairajan, R.E. White, Y. Podrazhansky, B.N. Popov, J. Power Sources 91 (2000) 122–129.
[31] B. Markovsky, A. Rodkin, Y.S. Cohen, O. Palchik, E. Levi, D. Aurbach, H.-J. Kim, M. Schmidt, J. Power Sources 119–121 (2003) 504–510.
[32] O.K. Park, Y. Cho, S. Lee, H.-C. Yoo, H.-K. Song, J. Cho, Energy Environ. Sci. 4 (2011) 1621.
[33] N.J. Dudney, T.N. Tiegs, J.O. Kiggans, Y-I. Jang, J.W. Klett, ECS Trans. 3 (27) (2007) 23–28.
[34] J. Xie, N. Imanishi, T. Zhang, A. Hirano, Y. Takeda, O. Yamamoto, J. Power Sources 192 (2009) 689–692.
[35] N.N. Bramnik, K. Nikolowski, C. Baehtz, K.G. Bramnik, H. Ehrenberg, Chem. Mater. 19 (2007) 908–915.
[36] J. Wolfenstine, U. Lee, B. Poese, J.L. Allen, J. Power Sources 144 (2005) 226–230.