

LiFePO₄ – 3 D carbon nanofiber composites as cathode materials for Li-ions batteries

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Abstract: The characterization of carbon nanofiber 3D nonwovens, prepared by electrospinning process, coated with olivine structured lithium iron phosphate is reported. The LiFePO₄ as cathode material for lithium ion batteries was prepared by a Pechini-assisted reversed polyol process. The coating has been successfully performed on carbon nanofiber 3D nonwovens 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 5 h under nitrogen. The surface investigation of the prepared composites showed a uniform coating of the carbon nonwoven nanofibers as well as the formation of cauliflowers-like crystalline structures which are uniformly distributed all over the surface area of the carbon nanofibers. The electrochemical measurements on the composites showed good performances delivering a discharge specific capacity of 156mAhg⁻¹ at a discharging rate of C/25 and 152mAhg⁻¹ at a discharging rate of C/10 at room temperature.

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1. Introduction

New phosphate based cathode materials LiMPO_4 (where $M = \text{Fe, Co, Ni, Mn}$) are considered to be strong candidates for use in advanced Li-ion batteries. For example LiFePO_4 (LFP) is developed as alternative positive electrode for lithium ion batteries in electrotraction [1-4]. However, the low electron conduction in LiFePO_4 is a major obstacle in such applications, especially to rapid Li-ion intercalation/deintercalation. To overcome this problem, carbon coatings are developed as a means to introduce an electron path [5, 6]. The carbon coating results are most efficient in increasing the conductivity of LiFePO_4 . The increase of electronic conductivity of LiFePO_4 surface provides a good rate performance at high discharging rate (C-rate) [7, 8].

The development of advanced electrodes for Li-ion batteries may benefit from porous structures of carbon made by electrospinning which is a simple and straightforward method of producing nonwoven mats of polymer nanofibers [9, 10]. A polymer or resin solution is supplied by a syringe pump through a needle connected to an electrode of a DC source and forms a droplet at the tip. When the electric potential reaches a critical level, the electrostatic Maxwell stress overbears the surface tension and viscoelastic forces and a polymer jet is issued. The jet is pulled by the electric stresses to a grounded counter-electrode, as well as undergoes a tremendous bending instability which results in a fractal-like jet path and a dramatic thinning of the jet [11]. In addition, solvent evaporates and a dry or semidry nonwoven polymer nanofiber mat is collected on the counter-electrode. Nanofibers made Polyacrylonitrile (PAN) [12-16] or phenolic resin [17, 18] can be converted in turbostratic carbon nanofibers nonwovens useful for the development of advanced batteries. Electrospinning can easily accommodate various

nanoparticles, for example, carbon black (CB) entrained into nanofibers to enhance their electrical conductivity [19].

Lee et al. [20] reported the preparation of LFP/C composites by adding the active material LiFePO_4 to a PAN solution to produce a blend with a PAN: LiFePO_4 ratio of 1:4, and then they electrospun it as nanofibers. They reported a discharge capacity of 153mAhg^{-1} measured at a discharging rate of 0.1C at room temperature for the LFP/C composites prepared without further annealing under inert atmosphere. On the other hand, Hosono et al. [21] reported preparation and characterization of a voluminous structure containing a multiwall carbon nanotube as a core element, the composite of LiFePO_4 and amorphous carbon as an inner shell, and an outer amorphous carbon shell. The carbon nanotube core oriented along the direction of the wire plays an important role in the electron conduction during the charge-discharge process, whereas the outer amorphous carbon shell suppresses the oxidation of Fe^{2+} . The authors reported a discharge capacity of 130mAhg^{-1} measured at a discharging rate of 0.1Ag^{-1} at room temperature.

A different approach to enhance the effects of the carbon content has been reported by Bhunasewari et al. [22], based on the addition of functionalized commercial carbon nanofibers (CNFs) during the sol-gel synthesis of LiFePO_4 . The authors found out that an oxidative wet functionalization of the CNFs by concentrated nitric acid results in a better adhesion of LiFePO_4 particles to their surface. Moreover, the additional surface of the carbon nanofibers offered an efficient method for increasing the interfacial area and decreasing the lithium ion diffusion distance. The latter allowed a fast charge transport and improved power capability (the specific capacity of 120mAhg^{-1} at a charge rate of 0.1C) compared to the acetylene black added LiFePO_4 even though the coating was not homogeneous.

In the present work, we report the investigation of novel composites, prepared by a straightforward Pechini-assisted sol-gel process. The composites consist of LiFePO_4 as cathode material deposited on carbon nanofiber 3D nonwovens prepared by electrospinning PAN+CB solutions. The composites have been characterized by SEM and electrochemical analyses. The electrochemical performances are discussed in relation to the structural and morphological investigation.

2. Experimental

Polyacrylonitrile (PAN; $M_w = 150$ kDa) was obtained from Polymer Inc. N-Dimethylformamide (DMF) anhydrous-99.8% was obtained from Sigma-Aldrich. 12 wt% PAN solutions in DMF containing 11-15 wt% of carbon black (CB) nanoparticles were electrospun and collected on a piece of aluminum foil as nonwoven nanofiber mats. After that, the nonwovens were teared out from the aluminum substrate and folded up into small rectangular 1×0.8 cm² pieces. Then, the fiber pieces were pressed hard between two glass slides. The resulting nonwoven pieces were placed in a furnace and stabilized in air for 30 min at 280°C, then carbonized in nitrogen at 1050 °C for 30 min (the ramp rate was 4 °C/min between the room temperature, 280, and 1050 °C plateaus). After that, the carbon nanofiber nonwovens were cut into small disks with the diameter of about 5-7 mm and thickness of the order of 1-2 mm.

The experimental procedures for the preparation and characterizations of the samples were similar to those reported earlier [23]. The composites were prepared by soaking the carbon nanofiber nonwovens in a starting aqueous solution containing lithium, iron and phosphate ions. The starting solutions were prepared by dissolving $\text{Li}(\text{CH}_3\text{COO}) \times 2\text{H}_2\text{O}$ (lithium acetate), $\text{Fe}(\text{SO}_4)_2 \times 7\text{H}_2\text{O}$ [iron(II) sulfate] in water as precursors (with the molar ratio 1:1) with citric acid (2 x mol [Fe]). After that, phosphoric acid in equimolar ratio with Li and Fe ions was added. 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. During this time the carbon nanofiber nonwovens have been fixed and kept into the solution. After cooling down the solution, the prepared composites were rinsed slightly with water and dried out by heating at 130°C for 24 h in vacuum. Finally, the samples were annealed at 600°C for 5 h.

The structural analysis of the samples was performed by X-ray powder diffraction using a D8 Bruker powder diffractometer (Cu $K\alpha_1$ + Cu $K\alpha_2$ 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 sample morphology. 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. The composites 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 (1M LiPF₆ in ethylene-carbonate: di-methyl-carbonate 3:7 (wt/wt), 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

The experimental set-up and the conditions of preparation of the carbon nanofiber nonwovens have reported in details elsewhere [9-13]. The important role played by carbon in the LFP-carbon composites is widely reported in literature. **Figure 1a** shows a typical SEM image of the carbon nanofiber nonwoven prepared by electrospinning of PAN with 15 wt% CB followed by carbonization at high temperatures. The nanofibers are fairly uniform in length and diameter,

some of them can appear brighter due to the electron-induced charging. Due to their high surface area they can be used as suitable substrate for the deposition of LiFePO_4 by using a simple sol-gel process. The LFP/C nanofibers composites have been prepared by placing the carbon nanofibers nonwovens into a starting solution containing Li^+ , Fe^{2+} and phosphates ions [23]. The solution has been heated up to 80°C and kept at that temperature for 2-4 h. After rinsing with water the composite was annealed under nitrogen atmosphere at 600°C for 5 h to form the LiFePO_4 phase as layer on the carbon nanofibers. The identification of the crystalline phase has been performed as previously reported in [23]. The XRD spectrum confirmed the presence of the olivine-like structured LiFePO_4 as major crystalline phase, crystalline reflections attributed to secondary phases have also been detected. Although a deeper investigation on the secondary phases has not been carried out, such peaks could belong, possibly, to Fe-poor phases (mostly $\text{Li}_4\text{P}_2\text{O}_7$) which usually appear during the decomposition of the LFP phase.

The micrographs of the LFP/C-nanofibers composites before and after annealing at 600°C for 5 h under nitrogen are shown in **Figure 1a-b**. The micrograph (**Figure 1b**) shows a uniform coating of the carbon nonwoven nanofibers as well as the formation of cauliflowers-like crystalline structures which are uniformly distributed all over the surface area of the carbon nanofibers. The size of the crystalline phase ranges between 0.5 and $2.5\mu\text{m}$, while the growth of the LiFePO_4 crystalline phase seems to occur at those locations at fiber surface area where the thermodynamic and kinetic conditions were favorable. The uniform distribution of the LiFePO_4 phase over the surface of the carbon nanofibers is a further confirmation of the morphological homogeneity of the carbon structure.

CV curves were recorded for the composites after annealing at $T = 600^\circ\text{C}$ for $t = 12$ h, using Li metal as counter and reference electrode and are shown in Figure 2. 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 deintercalation/intercalation potentials corresponding to the mean peak maxima as in Figure 2 are $3.55(\pm 0.01)V$ and $3.30(\pm 0.01)V$ respectively. The values clearly indicate that the CV profiles are reduplicate from the second cycle with a very slight difference from the first cycle.

The measurements indicate clearly an improved kinetics of the lithium deintercalation/intercalation processes in the composites annealed at $600^{\circ}C$. In fact, the peak voltage separation is $0.25(\pm 0.01)V$ in the first cycle and remains constant. This is probably due to the fact that lithium diffusion and electrochemical kinetics reach an optimal state from the beginning. However, the difference between oxidation and reduction potentials could indicate the presence of polarization occurring in the composites. This polarization 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.

The LFP/C nanofibers composites have been cycled [at least 20 times: erased] at different C-rates, C/25 and C/10 respectively. The higher loading was 37-39 wt % $LiFePO_4$ on carbon, a value which is in agreement with the data previously reported [24, 25]. The charge and discharge curves (in the voltage range between 2.5 and 4.0V) as a function of time, for the discharging rate of C/25 at room temperature are shown in **Figure 3a**. The voltage-capacity curves for the second discharging, for the discharging rates C/25 and C/10 are shown in **Figure 3b**.

The cycling curves as a function of time, shown in **Figure 3a**, are very similar to those reported in the literature. This indicates a very good reversible intercalation/deintercalation process into the composite confirmed by the high specific capacity of $156mAhg^{-1}$.

The discharge profiles, in **Figure 3b**, show slightly different profiles. The discharge profile measured at C/10 is noticeably curved, the 3.4 V voltage drops as the cell discharges due to polarization. This is due to the diffusion resistance within the composite electrode [26]. On the other site, a less curved profile can be observed by measuring at a discharging rate of C/25 that confirms the good quality of the sample. We can also observe that the specific capacity of the composites correspond to the 92% of the theoretical one (at C/25) and 89.5% (at C/10). This difference is relatively small compared to the values usually reported in the literature. A possible explanation of this could be (i) a high uniformity of the LCF/C nanowires composite as revealed by the morphological investigation; (ii) a high electronic conductivity of the carbon nanofibers (iii) a high “free” surface area of the carbon nanofibers. These last two factors could yield a determining contribution to the electrochemical performances of the composites. Further investigations are in progress to improve and optimize the electrochemical properties of the composites and to better understand the mechanisms determining them.

[erased]

4. Conclusions

In summary, we report the preparation and characterization of LiFePO₄/C-nanofibers composites obtained *via* a simple sol-gel process by electrospun nanofibers into a solution containing Li, Fe and phosphates ions. The surface investigation of the prepared composites revealed a uniform distribution of the LiFePO₄ crystalline phase over the surface area of the nanofibers. The electrochemical measurements of the composites revealed a discharge capacity of 156 mAhg⁻¹ and 152 mAhg⁻¹ at the discharging rates of C/25 and C/10 respectively at room temperature. A further investigation into the application of such novel composites as e.g. supercapacitor electrode material may also be promising.

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Captions for Figures

Figure 1 SEM micrographs (a) of carbon nanofibers prepared by electrospinning of PAN+15 wt%CB, and (b) of the LiFePO₄/ C nanofibers composites prepared by the assisted Pechini sol-gel method

Figure 2 Cyclic voltammograms recorded for LiFePO₄ / carbon nanofibers composites after annealing under nitrogen at T = 600°C for t = 12 h (scan rate 0.05 mVs⁻¹, in the potential range 2.5 - 4.4 V vs. Li⁺/Li).

Figure 3 (a) Charge and discharge curves (in the 2.5 – 4.0V range) vs. time, (b) voltage-capacity curves for the second discharging, measured at discharge rates of C/25 and C/10 and room temperature, for LiFePO₄ /C-nanofibers composites

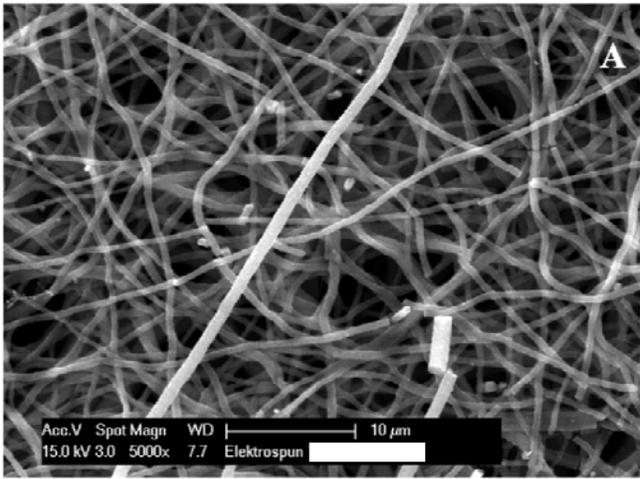


Fig. 1a

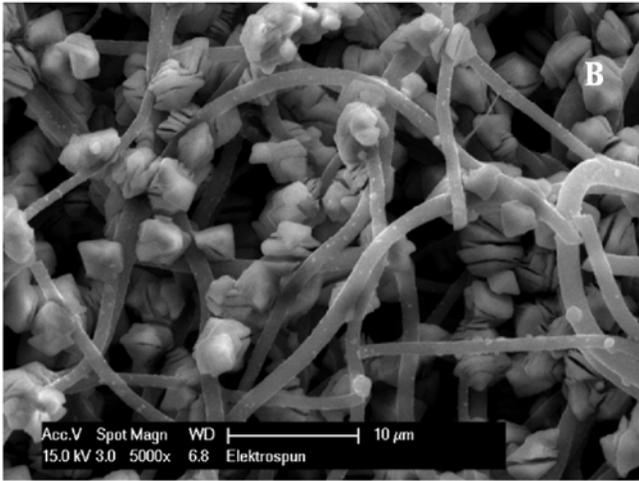


Fig. 1b

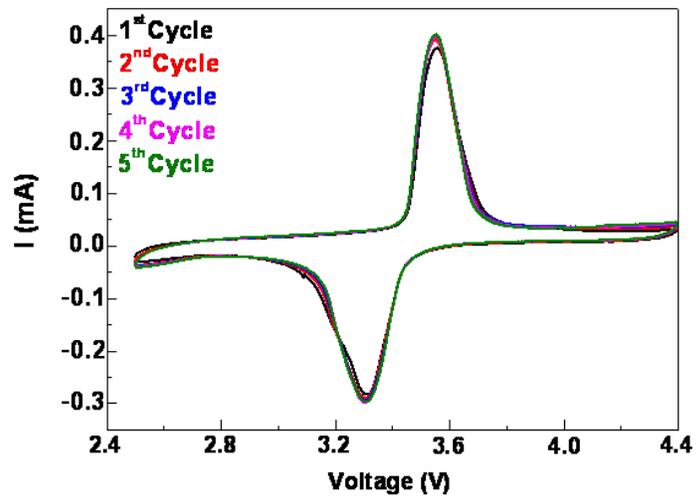


Fig. 2

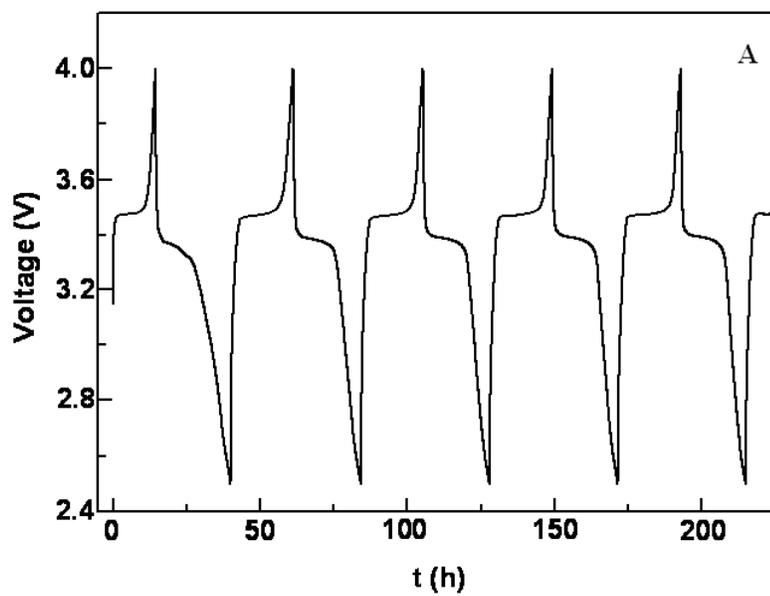


Fig. 3a

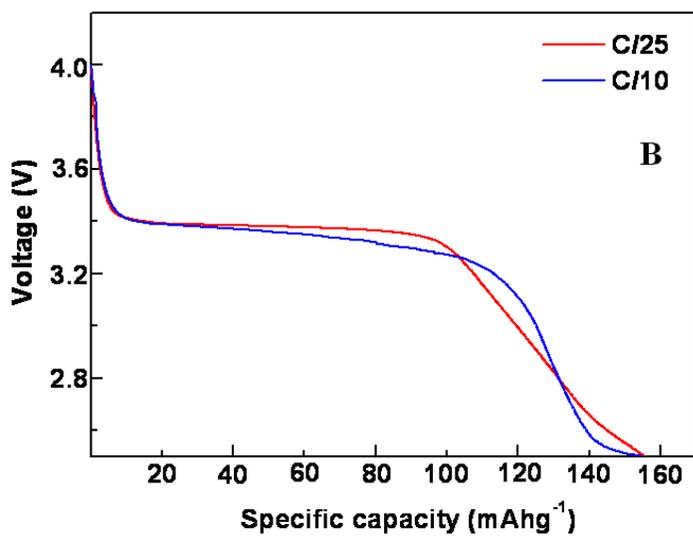


Fig. 3b