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Synthesis of $LiFePO_4$ nano-fibers for cathode materials by electrospinning process

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Nano-fibers of $LiFePO_4$ were synthesized from a metal oxide precursor by adopting electrospinning method. After calcination of the above precursor nano-fibers at 800 °C, $LiFePO_4$ nano-fibers with a diameter of 300 ~ 800 nm, were successfully obtained. Measurement were performed using X-ray diffraction (XRD), fourier transform infrared spectrometer (FT-IR), videoscope, scanning electron microscope (SEM) and atomic force microscope (AFM), respectively, were performed to characterize the properties of the as-prepared materials. The results showed that the crystalline phase and morphology of the fibers were largely influenced the starting materials and electrospinning conditions.

Key words: $LiFePO_4$, Nano-fiber, Electrospinning method, Lithium ion battery, Positive materials.

Introduction

Li-insertion compounds have been the subject of intensive research. A Li-insertion compound is a host for topotactic and reversible insertion and extraction of Li ions over a finite range of solid solutions. In a topotactic reaction, the host must be stable enough to tolerate repeated Li-insertion and extraction, the structure of the host is allowed to change only by atomic displacements with no diffusive rearrangement [1-5]. Among the known Li insertion compounds, layered rock salt systems, $LiCoO_2$, $LiNiO_2$, and the manganese spinel framework system $LiMn_2O_4$ are now used commercially as 4 V cathode materials in rechargeable lithium batteries. These third-row transition metals, M = Co, Ni, and Mn, which balance the Li^+ charge by the M^{4+}/M^{3+} redox reaction, generate 3 ~ 4 V vs. lithium [6, 7]. Recently, there has been considerable interest in developing olivine $LiFePO_4$ as a cathode material for high-power, large-scale applications such as electric vehicles. The overwhelming advantage of iron based compounds is that, in addition to being inexpensive and naturally abundant, they are less toxic than Co, Ni, and Mn. Also, the $Fe^{2+/3+}$ couple operates at around 3.45 V with a theoretical capacity of 170 mAh/g, providing an energy density comparable to those of layered $LiCoO_2$ and spinel $LiMn_2O_4$ cathodes. However, the key issue with $LiFePO_4$ is its one-dimensional lithium-ion diffusion and poor electronic conductivity (~10^{-9} S/cm) [8]. For such a reason, nanostructured materials are usually adopted to solve the kinetic problems associated with the solid-state diffusion of Li^+ intercalation and electronic conductivity [9-11]. Electrospinning is one of the best ways to make nano-material, It is a efficient fabrication method for preparing fibrous membranes composed of ultrafine fibers with a diameter of several micrometers to tens of nanometers. Electrospinning has the unique ability to produce nano-fibers of different materials with high specific surface area [12-15]. Also, there have been very few reports on the synthesis of cathode materials for lithium ion batteries by the electrospinning method. Thus, the purpose of the present article is to improve the morphology of $LiFePO_4$ nano-fibers obtained through a scalable nanofabrication process that is electrospinning. $LiFePO_4$ nano-fibers as cathode materials for lithium ion batteries have been prepared successfully from sol-gel precursors using the electrospinning method [16-18].

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Experimental

Synthesis

The solution for electrospinning was prepared from polyvinylpyrrolidone [PVP], deionized water, methanol [CH_3OH], nitric acid [HNO_3], lithium nitrate [$LiNO_3$], iron(II) nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$], and ammonium dihydrogen phosphate [$NH_4H_2PO_4$]. The mixture was stirred vigorously at room temperature for 24 hrs.

Electrospinning

The prepared solution was placed in a plastic capillary. The distance between the capillary and the collector was 15 cm, and the applied voltage was 15 ~ 20 kV. The nano-fibers were deposited on the collector, which was dried at 100 °C in a vacuum for 12 hrs. The dried fibers were calcined at 500 °C for 5 hrs in nitrogen to eliminate the organic residues. The product was recalcined at 800 °C in nitrogen atmosphere.

Characterization

X-ray diffraction patterns (XRD) for the cathodes

were obtained using a Siemens D-5000 diffractometer in the 2θ range from 10 to 70 ° with CuKα radiation (λ = 1.5409 Å). Infrared spectra were obtained using an FT-IR spectrometer with a resolution of 1 cm^{-1}, KBr wafers were used, and the weight percentage of nano-fibers in KBr was about 0.5%. The morphology of the obtained fibers was observed using videoscope (STV-ics 305B, SomeTech Vision) and scanning electron microscopy (Quanta 300), atomic force microscopy (XE - 100, Parksystems)

Results and discussion

Fig. 1 shows the XRD profile of $LiFePO_4$ nano-fibers synthesized at 800 °C. The XRD patterns of all the prepared nano-fibers show orthohombic structure (space group: pnma, 62). Commonly, the $LiFePO_4$ obtained by the heating process of the sol-gel method includes other phases such as Fe_2O_3 or Fe_2P. In this work, however, pure $LiFePO_4$ nano-fibers were obtained by using the electrospinning method, as can be deduced from the XRD pattern. The $LiFePO_4$ nano-fibers had unit cell parameters (Table 1) of a = 6.0072 Å, b = 10.3317 Å, c = 4.6907 Å and a cell volume of 291.12 $Å^3$. This result showed that, in comparison with other methods size of product is decreased, but only slightly.

Fig. 2 shows the FT-IR spectra of $LiFePO_4$ nano-fibers before calcination and after calcination. The FT - IR spectrum of the $LiFePO_4$ nano-fibers precursor (before calcination) shows bands around 1750 cm^{-1} (nitro-) and 3100 cm^{-1} (alkenes). After the $LiFePO_4$ nano-fibers were heat treated at 800 °C for 10 h, the organic band at ca. 1592 and 3100 cm^{-1} were obviously weakened. Notably, there existed 1450 and 3415 cm^{-1} peaks in both spectra in Fig. 2, which should be assigned to H_2O absorbed by the nano-fiber sample or the KBr wafers. These results illustrated that organic molecules could be removed completely from PVP/lithium nitrate/ iron nitrate/ammonium dihydrogen phosphate composite fibers when the calcinations temperature was above 800 °C.

The surface morphology of the precursor fibers mat was investigated by videoscope and the results were presented in Fig. 3. As can be readily seen, the fibers were randomly distributed on the collector. All fibers in the figure were investigated for both gel fibers in high viscosity and gel fibers in low viscosity. As shown in Fig. 3(b), (d), (f) (high viscosity), the precursor fibers

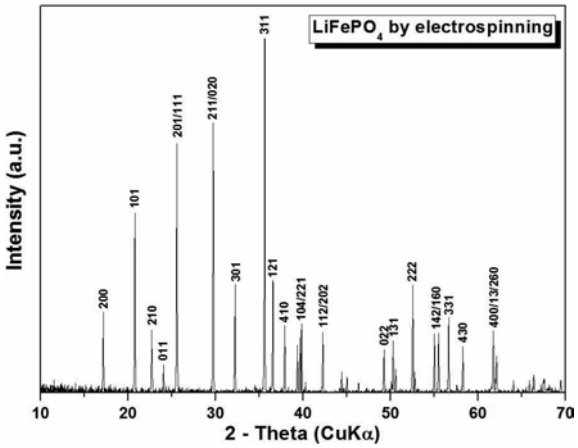

Fig. 1. XRD data for the obtained nano-fibers after cacination at 800 in nitrogen atmorsphere.

Table 1. Lattice parameters of $LiFePO_4$ synthesized at 800 °C.

Parameter	*Value*	*error*
a - axis	6.0072 Å	± 0.0004 Å
b - axis	10.3317 Å	± 0.0005 Å
c - axis	4.6907 Å	± 0.0002 Å
Cell volume	291.12 $Å^3$	± 0.02 $Å^3$

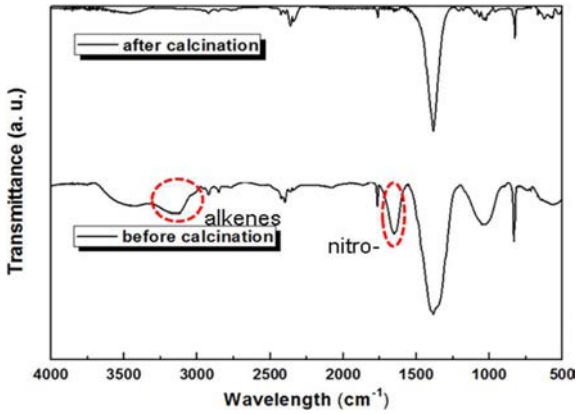

Fig. 2. FT-IR spectra of $LiFePO_4$ nano-fibers and precursor.

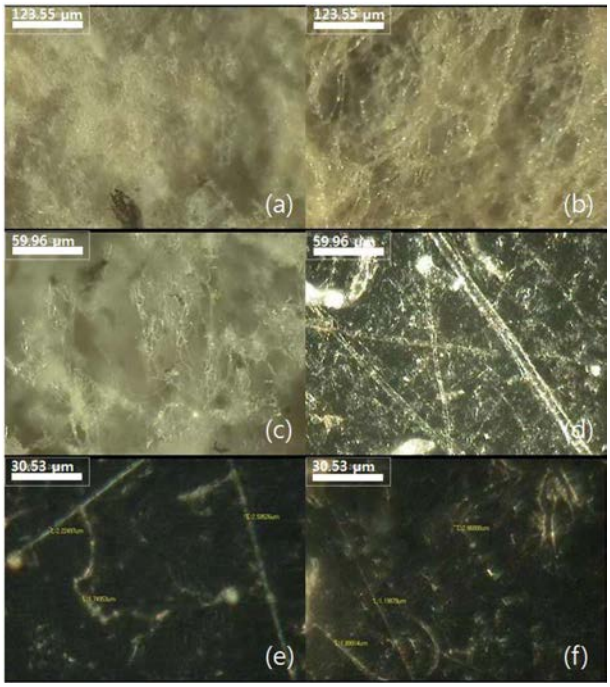

Fig. 3. Videoscope image of $LiFePO_4$ nano-fibers after electrospinning ; (a, c, e) fiber of low viscosity, (b, d, e) fiber of high viscosity

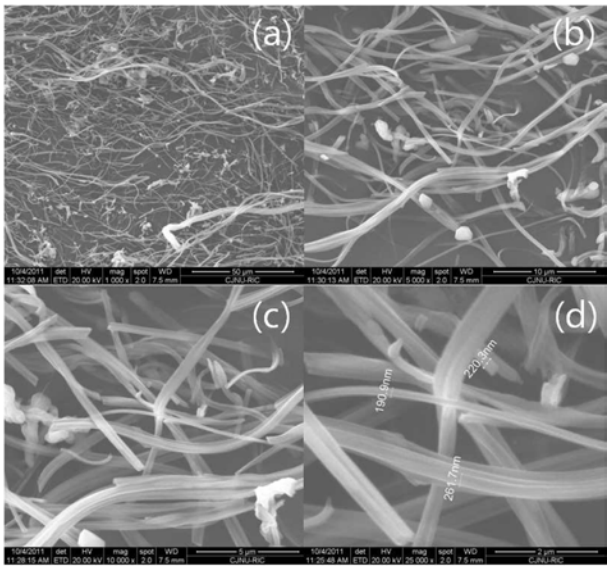

Fig. 4. SEM image of $LiFePO_4$ nano-fibers after calcination at 800 °C ; (a) x5,000, (b) x10,000, (c) x25,000 and (d) x50,000

appeared agglomeration. This result may be suggested due to increasing polymer for high viscosity.

Fig. 4 shows SEM images of the nano-fibers heated at 800 °C for 10 hrs. We could clearly investigate the agglomeration of $LiFePO_4$ nano-fibers after electrospinning by videoscope. Fig. 4 shows the SEM image of $LiFePO_4$ nano-fibers after calcination at 800 °C in a nitrogen atmosphere. From these images, we found improved fibrous morphologies with uniform diameter below 1 μm. Also, the agglomeration phenomenon was effectively eliminated through the calcination. As shown in images in Fig. 4, the nano-fibers structure is maintained, even if the sample was calcined at 800 °C for 10 h. The $LiFePO_4$ nano-fibers calcined in nitrogen had a diameter of approximately 100 nm ~ 800 nm, with a small amount of nano-fibers having diameters < 100 nm. From these results, our method was expected to achieve good electrochemical properties of nano-fibers by creating a well-defined morphology.

Fig. 5 shows the AFM image of $LiFePO_4$ nano-fibers. The diameter of the $LiFePO_4$ nano-fibers is found to be in the range of 100 ~ 600 nm. The $LiFePO_4$ nano-fibers are calcined at 500 °C in nitrogen to eliminate the organic residues. After calcination at high temperature, the surface of the $LiFePO_4$ nano-fibers become little aggregate and the diameter shows slight shrinkage. But, the original morphology feature of precursor fibers was maintained. It was considered the higher specific area to be a good influence on the electrochemical properties of cathode materials.

Conclusions

Nano-fibers of $LiFePO_4$ with calcined samples were synthesized using the electrospinning method. The XRD patterns of all prepared powders showed a orthohombic structure (space group : Pnma, 62). The prepared nano-fibers had diameters ranging from 100 ~800 nm. Even though sintering at high temperature, the original morphology feature of gel fiber was maintained. These kinds of materials are expected to have improving electrode properties due to its high surface area and 1D nano-structural properties.

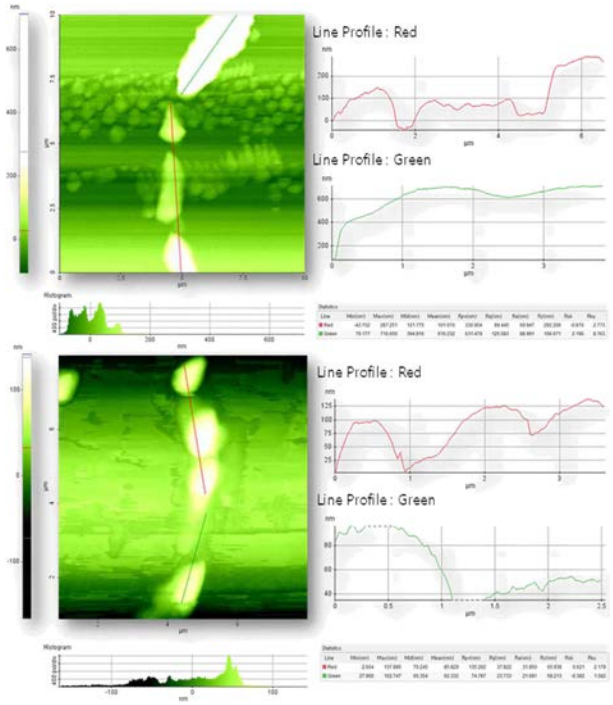

Fig. 5. AFM image of $LiFePO_4$ nano-fibers and diameter graph.

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