Electrospun Nanofiber Layers for Applications in Electrochemical Devices

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ABSTRACT

Low power and/or low energy density belong to main limiting parameters of electrochemical energy storage devices. Increasing of the surface area between an electrolyte and an active electrode material is the way how to improve their charging rate capability. By means of the Nanospider^{TM}technology prepared electrochemical materials can achieve a large specific surface area. Fibrous morphology, further, increases internal conductivity of the electrode and porosity improves transparency for ion mobility through electrode. These are other contributions of these materials to performance improvement. By means of the Nanospider^{TM}technology variety of electrochemically active materials for Li-ion batteries or supercapacitors can be prepared. The $Li_4Ti_5O_{12}$ spinel is an example of newly synthesized materials using electrospinning method. Due to zero-strain and fast lithium insertion this material is applicable as an anode in high rate and safety Li-ion batteries.

Keywords: lithium-ion battery, lithium titanate, anode, electrospinning

1 INTRODUCTION

Nowadays, electrospinning [1] as a simple and versatile strategy has been successfully employed in the preparation of various special inorganic materials such as cobalt oxide[2], nickel titanate[3] titanium oxide[4] or $LiCoO_2$ and $LiMn_2O_4$[5] as well as in fabrication of endless polymeric nanofibers. Production of inorganic fibers is achieved by spinning of mixture of ceramic precursor and polymer solution and consequential calcining in order to remove polymer template [6], [7].

One-dimensional fibrous nanostrutures of electrochemically active materials were suggested for design of advanced high rate and high power secondary battery due to high specific surface area, high permeability for electrolyte through the electrode and improved internal electronic conductivity. As materials for cathode of lithium-ion battery the electrospun spinel like $LiCoO_2$ and $LiMn_2O_4$ [5] were investigated whereas for anode the spinel lithium titanate ($Li_4Ti_5O_{12}$) was found as appropriate material [8].

The spinel $Li_4Ti_5O_{12}$ is an interesting material for anode due to its structural change resistance (zero-strain insertion material), fast lithium diffusion and high insertion potential vs. Li/Li^+. This parameters make in an attractive anode for high rate and safe battery application [9].

2 EXPERIMENTAL

The $Li_4Ti_5O_{12}$ fibers were electrospun from typical spinning solution. This was prepared by mixing of 16.5 g titanium tetraisopropoxide with 33 ml of acetic acid and 33 ml of ethanol. In addition the stechiometric amount of the lithium acetylacetonate (Li:Ti = 4:5) was diluted in solution. The solution was stirred for 10 min before being added into 82.5 ml of 6 % ethanolic solution of polyvinylpyrrolidone (PVP, M_w= 1300000g/mol). The solution was subsequently electrospun using the Nanospider^{TM} technology. The produced precursor nanofiberous layer was calcined in air at 750°C for 4 h.

The electrode for cyclic voltammetry measurement was prepared by means of the following procedure. The sample of spinel nanofibers was mixed with 4% aqueous solution of HPC (hydroxypropylcellulose). Resulting viscous slurry was deposited on conducting glass by the doctor-blading technique. The electrode was calcined in air at 450°C for 30 min. and afterwards was immersed into electrolyte consisted of 1 M $LiPF_6$ in a solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (volume ratio of 1:1) for electrochemical characterisation.

Morphology and size of lithium titanate fibers were observed by scanning electron microscope (SEM). The specific surface area was determined from nitrogen adsorption/desorption isotherms at liquid nitrogen temperature. The B.E.T method was used for surface area calculation. Crystalline phase of the fibers was identified by X-ray diffraction. The electrochemical properties were evaluated with a cyclic voltammetry (CV) at four different scan rates.

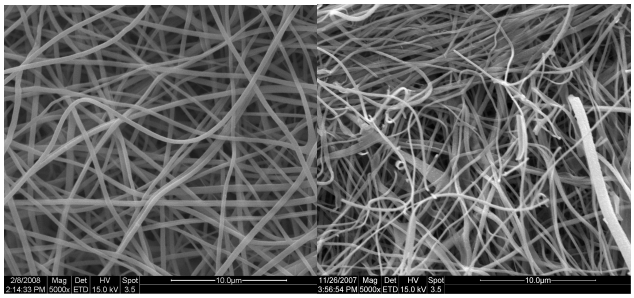

Figure 1: SEM images of electrospun lithium titanate precursor fibers before (left) and after (right) calcining.

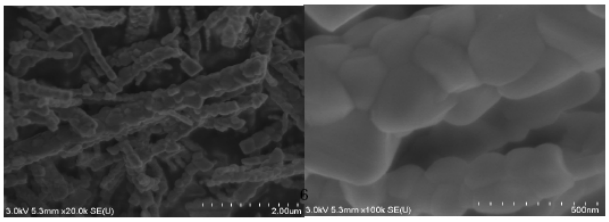

Figure 2: SEM images of calcined lithium titanate fibers with higher magnification.

3 RESULTS AND DISCUSSION

3.1 Morphology

The obtained fiber structure and morphology was analyzed before and after calcining by means of scanning electron microscopy. The SEM pictures are shown in Figure 1. As shown on these pictures the diameter of precursor fibers was found to be in range of 200-800 nm while the diameter of calcined fibres are in range of 100-500 nm, herewith the fiber structure kept unchangeable. By means of higher magnification was indicated that the calcined fibers were composed of small grains with size in range of 50-250 nm as shown in Figure 2. The specific surface area of calcined sample was examined using nitrogen sorption/desorption isotherm and the value calculated via B. E. T. model was found to be 40 g/m^2.

Figure 3 shows XRD pattern of the calcined precursor fibers. The diffraction pattern indicated the formation of a pure polycrystalline lithium titanate spinel after calcining procedure.

The electrochemical activity of prepared lithium titanate fibers was evaluated using the cyclic voltammetry at four different scan rate (0.1 - 1 mV/s). The resulted CV is shown in Figure 4. Cyclic voltammograms evidence well-developed spinel structure and excellent charge capacity of 174 mAh/g, which was calculated from anodic branch of CV with the slowest scan rate (0.1 mV/s).

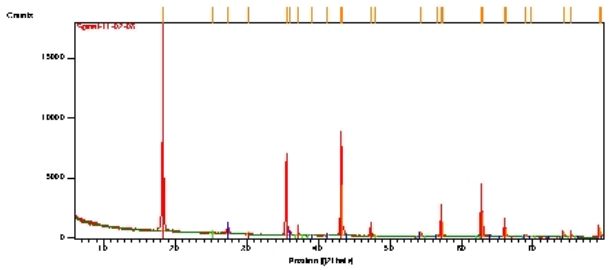

Figure 3: XRD patterns of $Li_4Ti_5O_{12}$ fibers

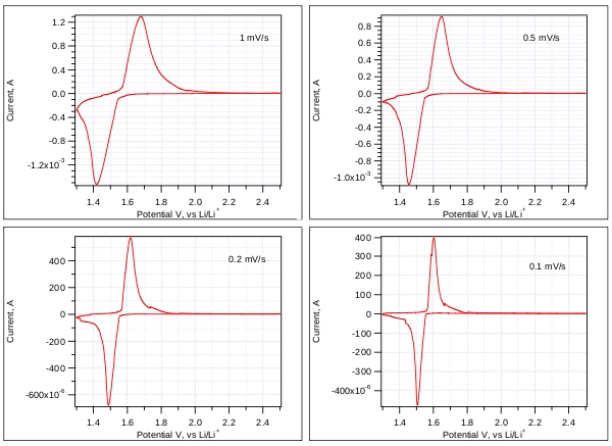

Figure 4: Cyclic voltammogram of Li insertion in lithium titanate spinel fibers. The electrode material was deposited on conducting glass as a support. Electrolyte: 1M $LiPF_6$ in EC/DMC (1:1, v:v)

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4 CONCLUSIONS

In summary, the ability of the Nanospider^{TM} technology to produce lithium titanate submicrometer fibers was demonstrated and their electrochemical properties as anode material for high rate rechargeable Li ion batteries have been examined by CV measurements. It should be emphasized that a simple and versatile method based on the Nanospider^{TM} technology for preparing nanofibers could be extended to other electrode materials of storage energy such as $LiCoO_2$ or $LiMn_2O_4$ and easily scalable upto industrial mass production.

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