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Nanostructured $LiCoO_2$ and $LiMn_2O_4$ fibers fabricated by a high frequency electrospinning

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Abstract

We have successfully prepared nanostructured $LiCoO_2$ and $LiMn_2O_4$ fibers using a novel high frequency electrospinning method. These fibers were composed of very small crystalline grains uniformly linked with an average size less than 100 nm. Scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and cyclic voltammetry (CV) were used to characterize their structures and electrochemical properties, respectively. These results suggested that a high frequency electrospinning was expected to be an effective method for the fabrication of inorganic composite fibers.

Keywords: Fibers; Nano-structure; High frequency electrospinning; $LiCoO_2$; $LiMn_2O_4$

1. Introduction

One of the recent themes to emerge from several high technology areas is focused on nanostructured materials including nanofibers, nanowires and nanotubes [1–3]. There are many synthetic techniques currently in use for their fabrications [4–6], for example, vapor–solid, vapor–liquid–solid, solution–solid, solvothermal routes, and electrospinning. Among these techniques, DC electrospinning has been widely recognized as a simply and versatile technique for the fabrication of microstructured materials for a variety of applications such as high surface area membranes, electronic devices, biomedical, and nanocomposite materials [7]. In general, a high electric potential at 5∼30 kV vs. a ground is applied to a polymer solution for charging liquid droplets in electrospinning process. At the meantime, a charged liquid droplet driven by Syringe pump is drawn out from the needle under the electric field to form a liquid jet. The continuous fibers ranging from less than 10 nm to over 100 nm in diameter are formed on the ground substrate. However, there is an inconvenience in some specialized applications to us a DC electrospinning technique. For example, the insulating materials cannot be used as the substrate in DC electrospinning process. In addition, electrostatic charging may result in the fiber instability or whipping in DC electrospinning [8]. Here, in order to explore new electrospinning methods, an attempt to use a high frequency instead of a static high voltage for the production of a non-woven fiber was made.

Tremendous interest currently focuses on the research and development of nanostructured ion batteries. Nanostructured electrodes could improve the energy density and rate capacity and insertion kinetics. It is widely believed that high surface area of cathode or anode materials could decrease solid-state diffusion path length. Three-dimensional (3D) structures were designed for a high rate and high power battery due to large interfacial areas of the cathode-separator-anode. Recently Horn et al. reported 3D structured lithium-ion batteries based on non-woven carbon fibers [9,10]. Apparently, the first step for the fabrication of 3D structured lithium-ion batteries is to prepare 3D structured nanofibers. As typical cathode materials used in recharge-

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able lithium batteries, $LiCoO_2$ and $LiMn_2O_4$ were promising cathode materials due to their relatively high energy densities [11–13]. However, there was no available report on the fabrication of these fibers. In this paper, we reported a high frequency electrospinning method to fabricate typical non-woven $LiCoO_2$ and $LiMn_2O_4$ fibers, and their structure and electrochemical properties were investigated.

2. Experimental

The schematic illustration of high frequency electrospinning apparatus used in this study was shown in Fig. 1, in which most of basic elements were similar to those of DC electrospinning system. It included a Syringe pump, a collector electrode, a source solution electrode and a high frequency generator. A high frequency electric field generator was applied to the outside of a N6 gauge needle, which was made of stainless steel with the inner and outer diameters of 0.6 and 0.8 mm, respectively.

The stoichiometric Li–Co–O/PVP(poly(vinylpyrrolidone), Aldrich, M_w=1,300,000) (Li:Co:PVP=2:2:1) sol was used as the electrospinning precursor solution to fabricate $LiCoO_2$ fibers, and was prepared by the following procedure: Briefly, 0.22 g (0.002 mol) lithium acetylacetonate ($Li(CH_3COCHCOCH_3$, Aldrich)) was dissolved in a solvent mixture composed of 3 mL ethanol and 0.5 mL acetic acids. Cobalt acetate (0.50 g (0.002 mol)) ($Co(CH_3COO)_2.4H_2O$, Aldrich) was dissolved in another 4 mL ethanol. After both of the lithium and cobalt precursors were mixed, they were added to 3 mL ethanol containing 0.11 g (0.001 mol) PVP, and were dissolved completely by using a magnetic stirring for nearly 30 min. Finally, an ethanol precursor solution containing 0.20 M PVP and 0.20 M Li–Co–O was obtained. Li–Mn–O/PVP sol with the stoichiometric ratio of Li:Mn:PVP=1:2:1 for the fabrication of $LiMn_2O_4$ fibers was also prepared by the similar routine. The frequency from a high frequency generator was fixed at 20 KHz. The discharge current of about 0.1 mA was formed along the tip of the needle and substrate when the outvoltage was about 6500 V. The syringe was moved at a speed of 5 cm/h. The fibers were collected on stainless steel substrate. The substrate was mounted at the distance of 2 cm from the tip of the needle. The substrate temperature was about 200 °C during the electrospinning process.

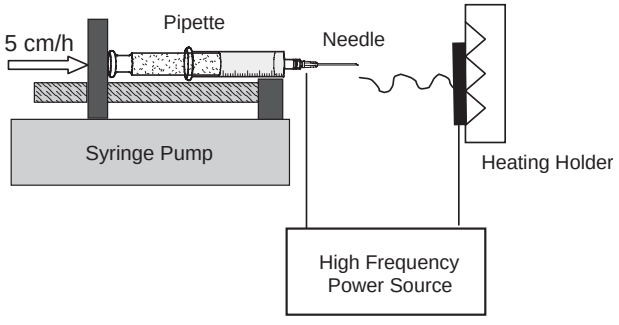

Fig. 1. Schematic illustration of the setup for a high frequency electrospinning.

X-ray diffraction (XRD) patterns and the morphology of the fiber samples were recorded by a Rigata/max-C diffractometer with Cu–K_α radiation and scanning electron microscopy (SEM) (Cambridge S-360), respectively. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) measurements were carried out by a 200 KV side entry JEOL 2010 TEM.

3. Results and discussion

When a high frequency generator was put on, the formation of electrospinning fibers could be observed by naked eye. Fig. 2(a) shows SEM images of these collected fibers by a high frequency electrospinning Li–Co–O/PVP sol. These fibers were randomly distributed on the substrate and their lengths could reach several micrometers. The average diameter of these fibers was found to be in the range from 1000 to 1800 nm, which was not classifiable as true nanofibers (diameter <100 nm). These fibers may consist of PVP and $LiCoO_2$. After burning the sample in air at 600 °C, the PVP was removed, a well-defined fiber texture kept unchangeable. As shown in Fig. 2 (b), their average diameter was found to be 1600±200 nm. These fibers were composed of very small grains uniformly linked with an average size less than 100 nm, indicating the nanostructure of the fibers. The diameter of the fibers could be varied by controlling the PVP concentration, the nozzle geometry and the speed of syringe. When the PVP concentration decreased to 0.05 M, the average diameters of the fibers before and after burning were around 500±100 nm as shown in Fig. 2(c) and (d). Meantime, we found that these fibers with small diameter were easily broken off after high temperature burning.

Similar results were also obtained for $LiMn_2O_4$ system as shown in Fig. 2 (e) and (f), in which Li–Mn–O/PVP sol was used. The average diameter of $LiMn_2O_4$/PVP composite was found to be about 950±100 nm. After burning in air 600 °C, the average diameter was reduced to be about 750±100 nm. The fibers exhibited a smooth surface and consisted of very small particles less than 100 nm (Fig. 2(f)). The size reduction of the fibers after burning could be due to the loss of PVP from the fibers and the crystallization, which has been confirmed by X-ray diffraction (XRD) and TEM measurements.

Fig. 3 shows XRD patterns of the calcined samples. Both calcined samples of $LiCoO_2$ and $LiMn_2O_4$ exhibited clear diffraction peaks. Three diffraction peaks appearing at 2θ=43.6°, 50.7° and 74.7° can be attributed to the stainless steel substrate. All the other *hkl* peaks can be indexed to the layered rock-salt structure of $LiCoO_2$ and the spinel structure of $LiMn_2O_4$, which represent the space group of trigonal symmetry R3m and Fd3m, respectively [14,15]. These results indicated the formation of a pure