Enhanced rate performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ fibers synthesized by electrospinning

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One-dimensional nano-structured spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with a diameter as thin as 50-100 nm was successfully prepared using electrospinning method followed by a heat treatment procedure. These nanofibers efficiently suppressed the large volume change and capacity fade inherent with bulk-sized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles when discharged to below 3.0 V, and thus demonstrated excellent rate capabilities in a voltage range of 2.0-4.8 V.

Abstract: Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) provides a high working potential as a cathode material for lithium-ion batteries. Yet there is a phase transition from cubic to tetragonal structure in LNMO during the $\sim 3\text{-V}$ charge/discharge region. To suppress the large volume change and capacity fade inherent with bulk-sized LNMO particles when discharged to below 3.0 V , one-dimensional nano-structured LNMO was prepared by an electrospinning method and a subsequent heat treatment. The well-separated nanofiber precursors combat the growth and aggregation of LNMO particles during the heating procedure and lead to improved capacity, better cycling stability, and improved rate capability of the final LMNO nanofibers. The as-prepared LMNO nanofibers have a diameter as thin as $50\text{-}100\text{ nm}$, which is the thinnest of this kind of complex compounds that contain multi-transition metal elements produced through the electrospinning method. In coin cell tests of this material at a current density of 27 mA g^{-1} , the initial discharge capacity was 130 mAh g^{-1} over a voltage range of $3.5\text{-}4.8\text{ V}$ and 300 mAh g^{-1} over a voltage range of $2.0\text{-}4.8\text{ V}$.

Keywords: electrospinning; nanofiber; high voltage spinel; cathode; lithium-ion battery

Introduction

Recently, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) has attracted extensive attention as a cathode material for lithium-ion batteries from many research groups due to its high operating voltage (4.7 V vs. Li/Li^+ ascribed to the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple) [1-8]. Another advantage of LNMO is that its spinel structure offers three-dimensional Li^+ -ion diffusion pathways that should lead to improved rate capability and cycling stability [7-9]. Since the reversible capacity of LNMO at the 4.7 V charge/discharge region is only 146 mAh g^{-1} , discharge to below 3.0 V has been investigated to incorporate the capacity contributed from the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple. However, the main problem at the ~ 3 V charge/discharge region is the phase transition from cubic to tetragonal structure, which leads to a large volume change. Obstructing this volume change and mitigating the resulting capacity fade is one of the greatest challenges to improving the LNMO performance over a wide voltage window.

Nano-sized particles accommodate more effectively the volume changes of electrode materials during the charge and discharge than bulk-sized particles. Two factors contribute to a high Li^+ -ions insertion-extraction rate in nanostructured materials. First, the high specific surface area results in a large interfacial reacting area in contact with the electrolyte. Second, the Li^+ -ion diffusion length in the solid-state phase is short enough to allow fast kinetics. For these reasons, controlling the nanostructure of electrode materials is of great importance in improving the performance of rechargeable lithium-ion batteries [10-17]. In the past few years, researchers have investigated the production of one-dimensional electrode materials by the electrospinning method to enhance capacity and reduce its fading with cycling [18-20]. Electrospinning is a well-known technique for producing polymer nanofibers [21-25]. By adding compounds to the polymer solutions, various researchers have used this technique to produce nanowires of V_2O_5

[26], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [27], TiO_2 [28], MnO_x [29], LiCoO_2 [30], LiFePO_4 [31, 32], etc. However, the challenge of maintaining the nanofiber structure during the heat treatment increases when the material to synthesize consists of more than one cation. Though $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiCoO_2 , and LiFePO_4 fibers were synthesized successfully, it is probably due to their comparatively low synthesizing temperature or to heating in an atmosphere without oxygen. When the heat treatment is performed in air and the temperature is higher than 600-700 °C, intense polymer decomposition and elemental oxidation result in a large amount of heat, which can destroy the electrospun fibers and break them to pieces [30]. For this reason, the synthesis of complex compounds that contain multi-transition metal elements through the electrospinning method is rare, and the diameter of the produced fibers is usually larger than 200 nm [33, 34].

We have produced LNMO nanofibers with a diameter as thin as 50 nm by using the electrospinning method followed by a heat treatment. In order to maintain the thin fiber structure, we finely tuned the heating procedure. Consequently, the growth and aggregation of LNMO particles have been dramatically suppressed during the heating, leading to the formation of well-dispersed nanofibers. With this unique 1-D structure, the as-prepared LNMO material demonstrated enhanced electrochemical performance with high capacities and rate capabilities in coin cell tests in the voltage range of 2.0 – 4.8 V. Electrospinning has the great potential to be an alternative approach to fabricate 1-D cathode materials containing multiple transition metals with well-defined nanostructure and, thus, improved Li-ion cell performance.

Experimental

Materials synthesis

High-voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanofibers were prepared by an electrospinning method followed by a heating process. The setup for electrospinning consisted of a high voltage supplier (Matsusada Precision, Japan), a syringe pump (Harvard Pump11, U.S.A.), and a plastic syringe equipped with a stainless steel needle. A carbon paper was used to collect the electrospun fibers. Two kinds of polymer solutions were prepared for electrospinning: 25 mg ml^{-1} PVP (poly(vinyl pyrrolidone, 1.3×10^6 MW) dissolved in methanol and 50 mg ml^{-1} PAN (polyacrylonitrile) dissolved in DMF (dimethylformamide). The metal compound starting materials dissolved in the polymer solutions included $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ from VWR. During the electrospinning process, the solution feeding speed was 0.12 ml/h, and the total acetate concentration in the polymer solutions was 0.12 M (Li:Ni:Mn:O = 2:1:3:8). The needle model used was 18G. Temperature was 25 °C in the room environment. Humidity was 22%. The applied electric field between the tip of the syringe and the carbon paper collector was 1.3 kV cm^{-1} for the PAN/acetate system and 1.0 kV cm^{-1} for the PVP/acetate system. To obtain the spinel phase of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanowires, the polymer/acetate composite precursor nanofibers underwent a heat treatment in air (described in Results and Discussion).

Characterization

The decomposition of the fiber precursor was investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The morphology of the as-prepared nanofibers and the electrodes was determined with a Hitachi S-4700-II scanning electron microscope (SEM). The X-ray diffraction patterns of the as-synthesized powders were collected on a D5000 Siemens X-ray diffractometer with Cu-K α radiation using a Cu-K α radiation source ($\lambda = 1.5406 \text{ \AA}$). Step size and dwell time were 0.02 ° and 1 s, respectively.

Electrochemistry

The as-synthesized LMNO nanofibers were made into cathode laminates, which were composed of 80 wt% active material, 10 wt% acetylene black, and 10 wt.% polyvinylidene difluoride (PVdF) binder. The laminates were dried at 120 °C overnight in a vacuum oven to remove the moisture. Electrode disks (9/16 in. in diameter) were punched out from the laminates for electrochemical testing. Coin cells (2032 type) were fabricated inside an argon-filled glove box. The anode was Li foil, the electrolyte was 1.2 M LiPF₆ in ethylene and ethyl methyl carbonate electrolyte (3:7 ratio by weight), and the separator was a polypropylene membrane (Celgard 2325). The cycling and rate performances were evaluated with a MACCOR battery cyler at room temperature.

Results and Discussion

The polymer/acetate fibers were successfully electrospun from the two polymer solutions: PAN/acetate dissolved in DMF solvent and PVP/acetate dissolved in methanol solvent. These two polymer solutions are widely adopted in the preparation of polymer fibers or polymer/compound composite fibers using the electrospinning method, which, in general, form fibers comparatively easily. We chose both of these two systems to obtain the proper system that can produce the finest LNMO nanofibers. These two polymer systems have different properties: the PAN/acetate in DMF solution was not as sensitive as the PVP/acetate in methanol solution to humidity in the environment during the electrospinning process, but its fibers were usually thicker because of the slower evaporation rate of DMF solvent as compared to methanol. To produce LNMO fibers, the addition of complex compounds into the polymer solutions greatly changes their original properties in the aspects of viscosity, evaporation rate and sensitivity to humidity, and therefore the electrospinning parameters should be tuned to obtain uniform thin

fibers. To produce uniform fibers without forming long leaf-shape beads, a high polymer concentration is preferred. By contrast, to produce fibers with a thinner diameter, a lower polymer concentration should be chosen. The optimal concentration of PAN dissolved in the DMF solvent is 50 mg ml^{-1} , which was used for this paper. The morphology of the electrospun fiber precursors is shown in Figure 1a. The fibers have a uniform diameter of 400 nm and a millimeter-scale length. Figure 1b shows that the fibers produced using the PVP/acetate dissolved in methanol solvent (25 mg ml^{-1}) had a uniform diameter of 100 nm and also a millimeter-scale length.

A subsequent heat treatment on the electrospun fiber precursors was required to complete the formation of the spinel phase. The main challenge in heating the polymer/acetate composite nanofibers is to maintain their one-dimensional structure and not to break the fibers into fragments. This difficulty results from the high polymer decomposition rate vs. the low diffusion speed of metal and oxygen elements. The different properties of the electrospun precursor fibers from the two polymer systems (such as thickness, density, and etc.) also affect whether these precursor fibers can withstand the subsequent heating process and still maintain the one-dimensional structure to form the final LNMO product. The thermal change of the electrospun precursor fibers from the two polymer systems during the heating process was analyzed by TGA and DSC. Figure 2 presents the TGA and DSC curves of the nanofiber precursors heated in air at a rate of 5 K min^{-1} . For the PAN polymer fibers without any metal compounds in it, the fibers underwent a huge weight loss after heating to above 600°C and left minor remains. A sharp exothermic peak at $\sim 300^\circ\text{C}$ and a broad exothermic peak at $\sim 570^\circ\text{C}$ were observed. The former was believed to relate to the reaction of dehydrogenation and cyclization of PAN [35]. The latter is related to the oxidation of PAN in the air. For PAN/acetate composite nanofibers, the

exothermic peak of PAN (at ~ 300 °C) became weaker compared to that of the pure PAN fibers, which was compensation from the endothermic process of acetate melting. The pure PVP nanofibers also had two exothermic peaks when heated in air (330 °C and 520 °C), which relate to the decomposition of PVP chains and the oxidation of the resulting small organic molecules [36]. For PVP/acetate composite fibers, the exothermic peaks also became lower because of the endothermic effect of the acetate. The endothermic peak at 750 °C corresponds to the formation of the spinel phase, indicating the fiber precursors needed to be heated above this temperature for the phase formation.

To prevent the breaking of the composite nanofibers at places where polymers burn out too fast to be replaced by the diffusion of metal and oxygen elements, a very slow heat treatment was necessary. Figures 3 and 4 show the morphologies of the PAN/acetate composite fibers under different heating rates in the middle and at the end of the heating process. In the first step, the fibers were heated to 600 °C (and were held at 300 °C, 400 °C, 500 °C, and 600 °C for 1 h each) at three rates: 1.6 °C min^{-1} , 1 °C min^{-1} , and 0.3 °C min^{-1} . Figure 3b shows that the fibers heated at 1.6 °C min^{-1} were broken to rods of several micrometers long. Those heated at 1 °C min^{-1} did not obviously break, but the nanofiber color was not uniform on the surface, indicating an uneven composition (Figure 3c). When heated at 0.3 °C min^{-1} , the composite fibers preserved their long and uniform structure, and these PAN/acetate composite fibers were then taken for the next step in the heating process, where the temperature was increased from 600 °C to 800 °C at different rates (1 °C min^{-1} , 0.5 °C min^{-1} , and 0.3 °C min^{-1} as shown in Figure 4b, c, and d, respectively); during the heat treatment, the temperature was held at 700 °C for 1 h and at 800 °C for 2 h. When the heating rate was not low enough, the fibers either melted (Figure 4b) or broke

(Figure 4c). At a rate of $0.3\text{ }^{\circ}\text{C min}^{-1}$ (Figure 4d), the obtained LNMO fibers were long and uniform, with a diameter of 200 nm.

In the other test series, PVP/acetate composite nanofibers easily preserved their structure at $2\text{ }^{\circ}\text{C min}^{-1}$ under $300\text{ }^{\circ}\text{C}$ heat treatment (as shown in Figure 5d). After being held at $300\text{ }^{\circ}\text{C}$ for 2 h, the fibers were heated to $800\text{ }^{\circ}\text{C}$ at different rates: $0.5\text{ }^{\circ}\text{C min}^{-1}$ (Figure 6b), $0.3\text{ }^{\circ}\text{C min}^{-1}$ (Figure 6c), and $0.1\text{ }^{\circ}\text{C min}^{-1}$ (Figure 6d). They were held at $400\text{ }^{\circ}\text{C}$, $500\text{ }^{\circ}\text{C}$, $600\text{ }^{\circ}\text{C}$, and $700\text{ }^{\circ}\text{C}$ for 1 h and at $800\text{ }^{\circ}\text{C}$ for 2 h. Fine LNMO fibers with a diameter of 50-100 nm were obtained at the rate of $0.1\text{ }^{\circ}\text{C min}^{-1}$.

Due to their thinner diameter, we chose the LNMO nanofibers obtained from heating the PVP/acetate fiber precursors for subsequent XRD characterization and cell fabrication. Figure 7a presents the XRD patterns obtained from these LNMO fibers. These diffraction peaks are characteristic of the cubic spinel structure (space group = $Fd\bar{3}m$, JCPDS #32-0581). An impurity peak at $2\theta = 22^{\circ}$ was probably due to trace impurity formed during heat treatment. These fibers were made into electrodes for cell tests. Figure 8b shows the surface morphology of the electrode, which was uniform and well mixed.

The LNMO nanofibers were electrochemically tested in coin cells with Li metal as the anode. Figures 8a and b show the charge-discharge voltage profiles, cycling performance, and rate capability of the cell within the voltage range of 3.5-4.8 V. The distinct charge-discharge plateau at 4.7 V is related to the redox reaction of $\text{Ni}^{2+}/\text{Ni}^{4+}$. The cell was cycled successively at currents of 27 mA g^{-1} , 54 mA g^{-1} , 108 mA g^{-1} , 216 mA g^{-1} , and then back to 27 mA g^{-1} again, five times at each current density. The initial discharge capacity of the cell was 130 mAh g^{-1} and declined to 85 mAh g^{-1} under the current density of 216 mA g^{-1} . When the current density was returned to 27

mA g⁻¹, the cell capacity was restored to 125 mAh g⁻¹. The first charge capacity was much larger than the first discharge capacity, resulting in a low initial coulombic efficiency. This is probably because of the side reactions between the nanofibers and the electrolyte due to their large contact area, which was also observed in other similar work [34].

Figures 8c and d show the charge-discharge voltage profiles, cycling performance, and rate capability of the high voltage spinel LNMO between the voltage range of 2.0 V and 4.8 V. A distinct plateau below 3.0 V was observed, which is related to the redox reaction of Mn³⁺/Mn⁴⁺. During this process, Li⁺ ions inserted into the available (16c) octahedral sites accompanying a simultaneous structure change from cubic spinel (*Fd3m*) to tetragonal spinel (*I4₁/amd*) [3, 37, 38]. The initial discharge capacity of the cell to 2.0 V was over 300 mAh g⁻¹ (current density = 27 mA g⁻¹). The discharge capacity under a current density of 216 mA g⁻¹ was 130 mAh g⁻¹, and when the current density was returned to 27 mA g⁻¹, the discharge capacity rose to 200 mAh g⁻¹. In other reports of the LNMO material[2, 37], bulk-sized particles show very poor electrochemical performance in the voltage range of 2.0 – 4.8 V due to the large volume change resulted from the structure transition in the process of lithium insertion/deintercalation in the ~3 V region. The nanofiber structure of our electrospun LNMO mitigated this volume change and enabled the discharge of LNMO to 2.0 V during cycling and rate tests. However, it should be noted that, in the voltage range of 3.5 – 4.8 V where LNMO does not have severe phase and volume change, the capacity improvement of the nanofiber structure was not obvious as compared with other structures.

Conclusion

Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanofibers with a diameter of 50-100 nm were fabricated by the electrospinning method with a subsequent heat treatment. Nanofibers were formed from both a PAN/acetate polymer solution and a PVP/acetate polymer solution. These fiber precursors were millimeter-scale long and had a diameter of 400 nm (PAN/acetate) and 100 nm (PVP/acetate). The polymer/acetate precursors preserved their nanofiber structure after undergoing a very slow heat treatment, and the obtained spinel LNMO fibers had a diameter of 200 nm (from PAN/acetate precursors) and 50-100 nm (from PVP/acetate precursors). The well-separated nanofiber precursors suppressed LNMO particle growth and aggregation during the heating procedure and led to high capacities and excellent rate capabilities of the final LMNO nanofibers. At a current density of 27 mA g^{-1} , the initial discharge capacity of the cell was 130 mAh g^{-1} (voltage range of 3.5-4.8 V) and 300 mAh g^{-1} (2.0-4.8 V).

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Figure Captions:

Figure 1 Morphology of electrospun composite fiber precursors produced from (a) 50 mg ml⁻¹ PAN and 0.12 M acetate dissolved in DMF and (b) 25 mg ml⁻¹ PVP/acetate dissolved in methanol.

Figure 2 Thermal properties of (a) PAN nanofibers, (b) PAN/acetate nanofibers, (c) PVP nanofibers, and (d) PVP/acetate nanofibers.

Figure 3 Morphology of (a) original electrospun PAN/acetate composite fibers and that of fibers heated to 600 °C under different heating rates: (b) 1.6 °C min⁻¹, (c) 1 °C min⁻¹, and (d) 0.3 °C min⁻¹. Temperature held at 300 °C, 400 °C, 500 °C, and 600 °C for 1 h.

Figure 4 Morphology of (a) electrospun PAN/acetate composite fibers heated to 600 °C, and that heated from 600 °C to 800 °C under different heating rates: (b) 1 °C min⁻¹, (c) 0.5 °C min⁻¹, and (d) 0.3 °C min⁻¹. Temperature held at 700 °C for 1 h and 800 °C for 2 h.

Figure 5 Morphology of (a) original electrospun PVP/acetate composite fibers and that of fibers heated to 300 °C under different heating rates: (b) 10 °C min⁻¹, (c) 5 °C min⁻¹, and (d) 2 °C min⁻¹. Temperature held at 300 °C for 2 h.

Figure 6 Morphology of (a) electrospun PVP/acetate composite fibers heated to 300 °C, and that heated from 300 °C to 600 °C under different heating rates: (b) 0.5 °C min⁻¹, (c) 0.3 °C min⁻¹, and (d) 0.1 °C min⁻¹. Temperature held at 400 °C, 500 °C, 600 °C and 700 °C for 1 h and 800 °C for 2 h.

Figure 7 (a) XRD patterns of the spinel LiNi_{0.5}Mn_{1.5}O₄ nanofibers prepared through electrospinning method with a subsequent heat treatment; (b) SEM image of surface morphology of the electrode made from LiNi_{0.5}Mn_{1.5}O₄ nanofibers.

Figure 8 (a) Charge/discharge voltage profiles and (b) cycling capacities vs. different current densities for spinel LiNi_{0.5}Mn_{1.5}O₄ nanofibers cycled between 3.5 V and 4.8 V; (c)

charge/discharge voltage profiles and (d) cycling capacities vs. different current densities for spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanofibers cycled between 2.0 V and 4.8 V.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Personal portrait photo and a biosketch

Dr. Rui Xu is currently a postdoctoral fellow at Argonne National Laboratory. She obtained her B.E. (2007) and M.S. (2009) in materials science and engineering from Tsinghua University in China, and her Ph.D. (2014) in materials science from University of Rochester. Her research is focused on advanced materials and cell configurations for high energy rechargeable battery systems, with an emphasis on next-generation Li-S battery development.

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