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Preparation and Characterization of Ultralong Spinel Lithium Manganese Oxide Nanofiber Cathode via Electrospinning Method

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ABSTRACT

Aim: ng at improving the high rate capability of spinel lithium manganese oxide ($LiMn_2O_4$) cathode, ultralong $LiMn_2O_4$ nanofibers are prepared by combination of electrospinning and sol-gel techniques. The effect of processing parameters, including the weight ratio of polyvinylpyrrolidone (PVP) to Li and Mn precursor, calcination temperature and time, on the morphology and the resultant cathode performance of spinel $LiMn_2O_4$ nanofiber cathodes have been systematically investigated. Thermal behavior of $LiMn_2O_4$ precursor nanofibers is performed on a differential scanning calorimetry-differential thermal analysis (DSC-DTA), indicating the spinel $LiMn_2O_4$ began forming at 513 °C. The cathode materials appear porous "network-like" morphology with nanosize in diameter (~170 nm), microsize in length (~20 μm) and pure spinel structure, confirmed by scanning electron microscopy (SEM) and X-ray diffractometer (XRD). The ultralong $LiMn_2O_4$ nanofiber cathode calcined at 700 °C for 8 h shows highest capacity and best rate capability. Its discharge capacity is 146 mAh g^{-1} at 0.1 C; more importantly, the discharge capacities are 112 mAh g^{-1}, 103 mAh g^{-1} and 92 mAh g^{-1} at high discharge rates of 10 C, 20 C and 30 C, respectively.

1. Introduction

In nowadays energy society, rechargeable lithium ion batteries utilize widely in portable electronics due to their high voltage, high specific energy, and long working life [1,2]. However, rapid charge and discharge characteristics are required for high power applications, e.g. hybrid electric vehicles (HEVs). In this regard, nano-sized cathode materials, possessing shorten diffusion path of lithium-ion together with extended the effective surface area and thus facilitating faster kinetics and higher rate capability, have gained great attraction. Comparing with varieties of layered Ni or Co oxide cathode materials, spinel $LiMn_2O_4$ is highly promising because of its low cost, high power density and environmental friendliness. However, it also suffers from considerable capacity fading on cycling due to structural degradation and poor rate capability. Substitution of Mn by transition metal element has performed to improve the cycle stability of spinel $LiMn_2O_4$ [3,4], whereas nano-sized $LiMn_2O_4$ cathodes have been investigated to improve the rate capability [5–10]. Among varieties of nanostructured $LiMn_2O_4$ cathodes, 1-D nanowire materials are considered to be most favorable structures, since faster kinetics and higher rate capability can be greatly facilitated by the efficient charge transport along their radius direction [6]. More importantly, previous research has shown that long nanowires with hundreds of micrometers in length can effectively prevent the self-aggregation after charge-discharge cycles [11], and can thus suppress the capacity fading and improve the cycling stability.

Compared with hydrothermal and solid state reaction method, electrospinning method is a relatively simple, inexpensive way to synthesize nanofiber cathode with controllable morphology by solution properties and other processing variables [12,13]. Ultralong V_2O_5 nanofiber cathode synthesized by electrospinning method yielded high initial discharge capacity (390 mAh g^{-1} between 1.75 V and 4.0 V, 275 mAh g^{-1} between 2 V and 4.0 V) [11] and the cyclic retention of the cathode was improved effectively due to its 1-D morphology that can increase the available electroactive surface area and inhibit self-aggregation [11,14]. The initial discharge capacity of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

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nanofiber cathode reached 173 mAh g^{-1} at 0.5 C. The calcination temperature was decreased to 700 °C compared with the solid state reaction method (typically higher than 800 °C) [15]. The Li-rich $Li_{1.2}Co_{0.17}Mn_{0.5}O_2$ nanofiber cathode exhibited good electrochemical performance, and its calcination temperature was also obviously decreased [16]. Electrospun $LiFePO_4$/carbon nanofiber cathode was also successfully fabricated to improve the electrochemical performance. The cathode exhibited high discharge capacity (above 165 mAh g^{-1}) at low rate (i.e. 0.05 C or 0.1 C) [17,18], excellent cycle performance (the capacity retentions were 93% and 94% after 500 cycles at 25 °C and 55 °C, respectively) and good rate capability (166 mAh g^{-1} at 0.1 C, 132 mAh g^{-1} at 5 C) [18]. The $Li_2Mn_{0.8}Fe_{0.2}SiO_4$/carbon composite nanofiber cathode was also prepared by electrospinning technique and its reversibility and cycling performance were improved effectively compared with $Li_2Mn_{0.8}Fe_{0.2}SiO_4$ powder [19].

The ultralong spinel $LiMn_2O_4$ nanofiber cathode of ~20 μm in length and ~150 nm in diameter with homogenous structure was successful synthesized by the electrospinning method, exhibiting superior cycling stability, rate capacity and lower degradation [20]. In this work, the effect of processing parameters in the electrospinning, including the weight ratio of PVP to Li and Mn precurcor, calcination temperature and time, on the morphology and the resultant cathode performance of spinel $LiMn_2O_4$ nanofiber were systematically investigated.

2. Experimental

Polyvinylpyrrolidone (PVP, Sinopharm) (Mw≈1300000) was dissolved in 20 mL ethanol under stirring as solution A. For $LiMn_2O_4$ precursors, lithium nitrate ($LiNO_3$, Sinopharm) and manganese (II) acetate tetrahydrate ($C_4H_6MnO_4 \cdot 4H_2O$, Sinopharm) were used as starting materials and dissolved in 20 mL deionized water with a stoichiometric ratio of 1:2 as solution B. Then the solution A and B were mixed together for electrospinning. Three weight ratios of PVP to $LiMn_2O_4$ precursors were investigated; the concentrations of PVP and $LiMn_2O_4$ precursors in the mixed solution (S1, S2 and S3) were shown in Table 1.

These three solutions were delivered in a 20 mL syringe with a metal needle of 1.4 mm in diameter at a constant flow rate of 0.4 mL h^{-1}. The metallic needle was connected to a high-voltage power supply (15 kV). A piece of grounded aluminum foil was placed vertically, and the distance between aluminum foil and the tip of the needle was 12 cm. The precursor nanofibers formed by rapid evaporation of solvent. To fabricate $LiMn_2O_4$ nanofiber cathodes, the precursors were heated at 400 °C for 4 h in air first, and then calcined at 650 °C, 700 °C and 750 °C for different time in air, respectively. All of the heating rates were 1 °C min^{-1}.

The morphology of the precursors and the resultant cathodes were investigated by field emission scanning electron microscope (FESEM, Zeiss SuprATM 55 microscope). The crystal structures of the samples were analyzed by X-ray diffraction (XRD, Rigaku RINT2400 with Cu Ka radiation, λ=1.5405 Å) in a 2θ range of 10°-80°. Thermal analysis of the precursor was performed on a differential scanning calorimetry/differential thermal analysis (DSC/DTA, SETARAM) at a heating rate of 10 °C min^{-1} in air.

The electrochemical tests were carried out on CR2032-type coin cells. The cathodes were prepared by mixing 75 wt% $LiMn_2O_4$, 15 wt% super carbon and 10 wt% Polyvinylidene fluoride with the help of 1-methyl-2-pyrrolidone and pressing on an aluminum foil. The anode was a piece of lithium metal. The electrolyte consisted of 1 M $LiPF_6$ in a mixture of ethylene carbonate and dimethyl carbonate (volume ratio 1:1). The charge and discharge characteristics of the cathodes were performed on LANHE test system at various current rates (0.1-30 C, 1 C = 148mA hg^{-1}) in the range of 4.3-2.6 V versus Li/Li^+.

Table 1
Concentrations of PVP, $LiMn_2O_4$ precursors and solvents in mixed solutions.

Sample No.	PVP (wt%)	$LiMn_2O_4$ precursors (wt%)	Solvents (wt%)
S1	6	3	91
S2	6	6	88
S3	6	12	82

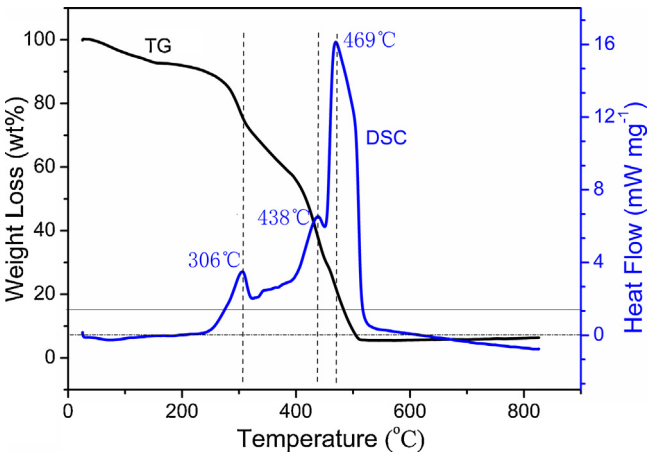

Fig. 1. DTA-DSC curves of $LiMn_2O_4$ precursor nanofiber from S2: PVP/$LiNO_3$/$C_4H_6MnO_4$ composites.

3. Results and discussion

3.1. Microstructural characterization

3.1.1. Thermal behavior of $LiMn_2O_4$ precursor nanofiber

Fig. 1 shows the thermal behavior of $LiMn_2O_4$ precursor nanofiber from S2. DTA curve shows that the continuous weight loss of the precursor nanofiber started at about 42 °C and terminated at about 513 °C, and four regions of weight loss were observed at about 80 °C, 306 °C, 438 °C and 469 °C, respectively. As shown in the DSC curve, the broad endothermic peak at about 80 °C was considered to be the loss of absorbed water. The exothermic peak at about 306 °C was assigned to the decomposition of lithium nitrate and manganese acetate, and the transitional product of $LiMn_2O_4$ was formed at the same time. The exothermic peaks at about 438 °C and 469 °C were ascribed to the degradation of PVP side chain and main chain, respectively, and the transitional product began to transform into spinel $LiMn_2O_4$. When the temperature was up to about 513 °C, there was no thermal reaction peak in heat flow and no change in weight loss, indicating that the PVP was completely degraded and the pure spinel $LiMn_2O_4$ was fabricated.

3.1.2. Morphology of $LiMn_2O_4$ precursor nanofibers and $LiMn_2O_4$ nanofiber cathodes

The morphologies of precursor nanofibers prepared by electrospinning from S1, S2 and S3 are shown in Fig. 2(a), (b) and (c). They exhibit smooth surface and round shape with nano-sized diameter and micron-grade length, forming "network-like" structures. The average diameters of the precursor nanofibers are increased slightly with increasing concentrations of $LiMn_2O_4$ precursors, yielding ~300 nm, ~350 nm and ~400 nm, respectively. The morphologies of $LiMn_2O_4$ nanofiber cathodes calcined from S1, S2 and S3 at 700 °C for 8 h are shown in Fig. 2(d), (e) and (f), respectively. The nanofiber structures are still maintained. In addition, with increase of concentrations of $LiMn_2O_4$ precursors, the average diameters of $LiMn_2O_4$ nanofiber cathodes increase