



Binder-free carbon fiber-based lithium-nickel-manganese-oxide composite cathode with improved electrochemical stability against high voltage: Effects of composition on electrode performance



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ABSTRACT

A binder-free nickel-manganese-based cathode is developed using carbon fibers as current collector via a low-temperature sequential process including electrodeposition, hydrothermal reaction, and calcination. The physical and electrochemical properties of the fiber-type cathodes are found to depend significantly on the Mn:Ni molar ratio and calcination temperature. The typical cathode material exhibits flake-like morphology and is composed of spinel LiMn_2O_4 (LMO), $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO), and lithium-rich layered Li_2MnO_3 (LRL-LMO), forming an LMO/LNMO composite. During electrochemical evaluation under high voltage operation at 2.5–4.9 V, the fiber-type LMO/LNMO cathode shows discharge capacity of $\sim 140 \text{ mAh g}^{-1}$ with enhanced discharge voltage and stable cycle performance with over 98% capacity retention after 50 cycles. The capacity of fiber-type LMO cathode decays from 120 mAh g^{-1} with cycling (2.5–4.9 V), and begins to fail at the 12th cycle. Hence, the spinel LNMO can function as a framework to stabilize the LMO/LNMO composite material against high voltage. Fiber-type LMO/LNMO cathode benefits from the integrated electrochemical characteristics of spinel LMO, LNMO, and LRL-LMO, leading to improved electrode performance.

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1. Introduction

The lithium ion battery (LIB) is more attractive than other secondary batteries such as lead–acid, Ni–Cd, and Ni–MH in the current energy storage market for portable electronic devices such as smartphones, tablets, and laptops [1–4]. LIB possesses higher energy density, power density, and longer cycle life, enabling it to be a promising rechargeable battery [5]. Large-scale batteries are required to meet the increasing demands of transportation applications such as electric vehicles (EVs), hybrid electric vehicles (HEVs), and other stationary energy storage systems. It is still a challenge to develop large-scale LIBs with high energy and power density at low cost since battery performance is mostly determined by the intrinsic properties of cathode materials [6]. Olivine-type LiFePO_4 has been widely studied and commercialized as a cathode material for LIBs due to its favorable thermal and cycling stabilities. Its energy density of $\sim 500 \text{ Wh kg}^{-1}$ does not satisfy the energy storage requirement for large-scale batteries [7]. Lithium-

rich layered oxides attract attention because they can deliver more energy density than the olivine-type; however, voltage decay upon cycling is inevitable [8]. A typical lithium-rich layered cathode material like Li_2MnO_3 (LRL-LMO) presents poor cycle performance due to phase transformation from the layered structure to spinel, which limits its usage in practical LIBs [9]. Spinel-type $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) is considered a promising candidate among cathode materials because it has high working voltage corresponding to an energy density of 658 Wh kg^{-1} [10], satisfactory cycling stability, and rate capability [11–14]. Despite the aforementioned advantages, the specific capacity of this spinel material is around $120\text{--}130 \text{ mAh g}^{-1}$, which is not favorable for large-scale energy storage applications. For electrode fabrication, the cathode is prepared based on a conventional fabrication technique in which a tape casting process is necessary. This mechanical process limits electrode design and is not adequate for flexible battery development. A slurry of the active materials with additives such as binders and conductive agents is commonly used for tape casting. The additives can improve the electrical conductivity of the electrode by forming a solid connecting network in the active material, whereas they do not contribute to electrochemical capacity, thus sacrificing

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energy density. A trade-off exists between energy and power density associated with an inverse relationship [15]. Solvent *N*-methyl-2-pyrrolidone (NMP) used to prepare the slurry is costly and harmful [16], having impacts on our ecology and environment. To avoid the above disadvantages, an electrode structure design that can render a direct connecting network while reducing the amounts of additives and solvents is expected [17,18]. As a new electrode design, carbon fibers have been used as current collectors for preparing a LiFePO₄ cathode [19]. In the reported electrode fabrication process, commercial LiFePO₄ material was directly coated onto the fibers without additives. This fiber-type LiFePO₄ cathode demonstrated improved electrode performance in terms of cycling stability and rate capability. Fiber-type electrodes have been successfully developed for use in secondary batteries including the Ni–MH battery [20,21], LIB [22–26], and sodium ion battery (NIB) [27–29]. Unlike the coating method, fiber-type Li–Al–Mn–O [22], LiMnO₂/LiMn₂O₄ (LMO) [24], and lithium-rich LMO [25] cathodes can be prepared via a two-step low-temperature process—the first step being electro-deposition and the second hydrothermal reaction—without using additives and solvents. These fiber-type cathodes possess satisfactory electrode performances, which can be precisely evaluated without the influence of additives. Most active materials for fiber-type cathodes are based on a single compound. To further enhance the electrode performance, the development of a fiber-type cathode consisting of multiple active material components (i.e. a composite) should be considered.

We attempted to develop a fiber-type nickel-manganese-based (LMO/LNMO) cathode that integrates the advantages of both lithium-rich layered and spinel materials. The cathode material is synthesized via a sequential low-temperature process including electrodeposition, hydrothermal reaction, and calcination without using additives and solvents. The morphologies, crystal structures, and electrochemical characteristics of the synthesized materials—corresponding to various synthesis conditions—are discussed. The fiber-type LMO/LNMO composite cathode exhibits improved electrode performance (relative to the fiber-type cathode consisting of single active material of lithium-manganese-oxide (LMO)) in terms of capacity and cycling stability under high voltage operation.

2. Experimental

2.1. Preparation procedures for fiber-type LMO/LNMO cathode

As the first step for preparing the fiber-type cathode, a carbon fiber-tow (Formosa Plastic Corporation) containing 12,000 single fibers was dipped in 0.3 M M(NO₃)₂ (M=Ni + Mn) (Panreac AppliChem) solution for electrodeposition. The Mn:Ni molar ratio in the solution was varied from 8:2 through 7:3 and 6:4 to 5:5 as an experimental parameter. The electrochemical reaction was driven using a DC power supply (GPS-4303, GW Instek) under galvanostatic operation at current density of 2.5 mA cm⁻² at 25 °C. After 30 min reaction, a precursor layer was coated onto the fibers. The precursor fibers were then moved to a stainless steel autoclave containing LiOH (Panreac AppliChem) solution to perform hydrothermal reaction at 100 °C for 20 h, followed by cleaning, drying, and then calcining at 300 °C or 400 °C for 1 h. A synthetic material layer was coated onto the fibers, forming a fiber-type cathode. The synthesis process is schematically summarized in Fig. 1. The obtained active material loading was 8 mg cm⁻² on average, which was estimated based on the apparent surface area of the cathode after drying at 100 °C for 1 h. The mass loading was comparable to those previously reported for LNMO electrodes [30,31].

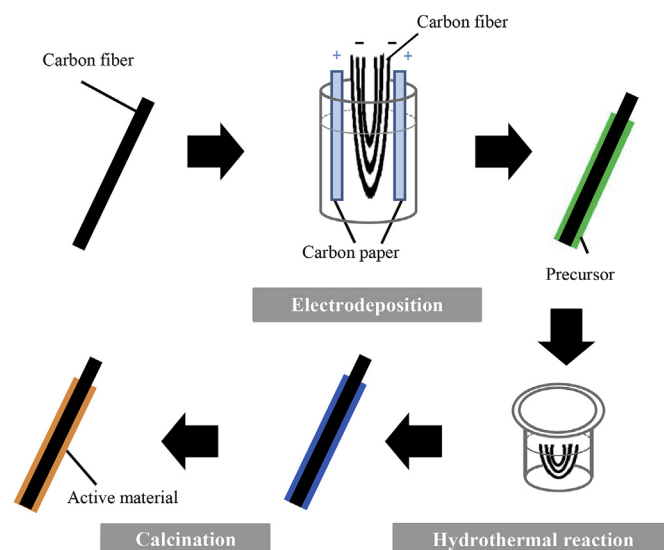


Fig. 1. Schematic diagram for the simplified synthesis process of fiber-type cathodes.

2.2. Material characterization

Thermogravimetric and morphological analyses of carbon fibers and fiber-type cathodes were carried out using a thermogravimetric analyzer (TGA) (Q-500, TA) and a scanning electron microscope (SEM) (S-3000 N, Hitachi, Ltd.), respectively. The crystal structures of the cathode materials were investigated by X-ray diffraction (XRD) using an X-ray diffractometer with Cu-K_α radiation (D8 Advance, Bruker AXS) between 10° and 70° at scan rate of 3° min⁻¹. Raman spectra of various samples were obtained via a Raman spectrometer (iHR550, Horiba JOBIN Yvon) with incident laser excitation at 532 nm.

2.3. Electrochemical evaluation

A coin-type test cell (CR2032) was used to carry out the galvanostatic charge/discharge tests to evaluate the electrochemical performances of the fiber-type cathodes. The fiber-type cathode—cut to a moderate length of 0.5 cm—was placed in the cell with its two ends contacting the metal cap of the cell. A lithium metal foil and glass filter served as the counter electrode and separator, respectively. The electrolyte used was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) in the ratio 1:1 (v/v) (HOPAX). Cell assembly was completed in a glove box under an argon-filled environment. Cyclic voltammetry (CV) was carried out using a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie) to investigate the redox behaviors of the fiber-type cathodes during electrochemical tests. The electrochemical investigations were conducted at 25 °C.

3. Results and discussion

3.1. Physical properties of fiber-type cathodes prepared under various conditions

Fig. 2 shows thermogravimetric analyses of the carbon fiber and typical fiber-type cathodes. The weight of the carbon fiber remained until the temperature reached 600 °C and then it significantly decreased with increase in temperature to 900 °C, where the carbon fiber almost lost its weight. The synthesis temperature of active material on carbon fibers should not exceed

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