Hollow lithium manganese oxide nanotubes using MnO_2-carbon nanofiber composites as cathode materials for hybrid capacitors

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ABSTRACT

To improve the electrochemical performance of hybrid capacitors, hollow lithium manganese oxide ($LiMn_2O_4$, LMO) nanotubes (NTs) as cathode materials were synthesized by a solid-state reaction, using MnO_2 coated on a porous carbon nanofiber (PCNF) templates. To determine the optimum shell thickness of hollow LMO, the time of MnO_2 coating on PCNF was adjusted to 10, 30, and 60 min. Among these, hollow LMO NTs, which were synthesized by 30-min coating with MnO_2 on the PCNFs, have superior performance. They exhibited an excellent reversible capacity (~72.8 mAh g^{-1}) at 1 C, capacity retention of ~98.4% after 100 cycles, and an excellent high-rate capability. This superior performance can be explained by the hollow structure giving a reduced diffusion distance for Li-ions, the networked structure of one-dimensional NTs allowing fast charge transfer, and the achievement of the optimal stoichiometric ratio of the LMO phase.

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1. Introduction

Hybrid capacitors (HCs) have received considerable interest for use in various applications such as portable electronics, electric cars, and generators [1–3]. One type of HC, lithium-ion capacitors (LICs), combining the advantages of lithium-ion batteries (LIBs) and electric double-layer capacitors (EDLCs), have recently been investigated for applications requiring high energy density and high power density simultaneously [4–6]. LICs are composed of an anode, a cathode, a separator, and an electrolyte. Among these, the choice of cathode material, for example $LiCoO_2$ (LCO), $LiNiO_2$ (LNO), or $LiMn_2O_4$ (LMO), directly affects the electrochemical performance of LICs [7,8]. LMO is particularly attractive as a cathode material for various reasons including its high theoretical capacity (~148 mAh g^{-1}), high power density, and low cost [9–11]. However, it suffers from capacity fading during cycles and a poor rate capability due to structural degradation. From a morphology perspective, one-dimensional (1-D) nanostructures such as nanowires, nanorods, and nanobelts have recently been receiving considerable attention because they possess unique structures with relatively large surface-to-aspect ratios and demonstrate efficient charge transport pathways [12]. The preparation of LMO 1-D nanostructures, has been attempted by various synthetic methods including a

precipitation method, a microemulsion method, and a solid-state method. For example, Meng et al. synthesized 1-D LMO nanowires using a precipitation method, which exhibited a reversible capacity of ~63 mAh g^{-1} and capacity retention of ~70.4% after 50 cycles at 0.2 C [13]. Cheng et al. fabricated LMO nanorods by a microemulsion-based method and a solid-state reaction, which showed the reversible capacity of ~57 mAh g^{-1} and capacity retention of ~86.0% after 500 cycles at 10 C [14]. Despite these efforts, the development of hollow LMO nanostructures for hybrid capacitors has not yet been reported. This hollow nanostructure has the unique properties of the reduced the diffusion length of Li-ions and alleviation of volume expansion, which can cause the improvement of electrochemical performances for hybrid capacitors [15,16]. In this study, we synthesized hollow LMO NTs using MnO_2 coated on a porous carbon nanofiber (PCNF) template by means of electrospinning, direct redox reaction, and a solid-state reaction. We used these to demonstrate the correlation between their structural properties and electrochemical performance as cathode materials.

2. Experiments

2.1. Synthesis of hollow lithium manganese oxide ($LiMn_2O_4$, LMO) nanotubes (NTs)

Hollow $LiMn_2O_4$ (LMO) nanotubes (NTs) were synthesized by a

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solid-state reaction using MnO_2-coated porous carbon nanofibers (PCNFs) as a template. The MnO_2-coated PCNF templates, which are crucial for formation of the desired hollow structures, were prepared by a combination of electrospinning and direct redox reaction. The PCNFs were obtained using electrospinning. Firstly, 10 wt% polyacrylonitrile (PAN, $M_w = 150,000$ g mol^{-1}, Aldrich) and 0.5 wt% poly (styrene-co-acrylonitrile) (SAN, $M_w = 165,000$ g mol^{-1}, Aldrich) were dissolved in N,N-dimethylformamide (DMF, Aldrich). Subsequently, the prepared solution was loaded into a syringe equipped with a 23-gauge needle. The feeding rate and the distance between the needle and collector were fixed at ~0.03 mL h^{-1} and ~15 cm, respectively. To collect the spun nanofibers, a working voltage was applied of ~13 kV using a DC power supply (Powertron. Co. Ltd, Korea). The nanofibers were then stabilized at 280 °C for 2 h in air before carbonizing at 800 °C for 2 h in an N_2 atmosphere. The MnO_2 coating was added by a direct redox reaction, performed by mixing two solutions. One of the PCNFs dispersed in 2.0 M H_2SO_4 and the other of $KMnO_4$ dissolved in DI-water. The mixed solutions were reacted at 80 °C, the reaction time was varied to 10, 30, or 60 min to obtain different MnO_2 layer thicknesses on the PCNFs. Finally, the MnO_2 coated PCNFs were washed using DI-water and dried at 80 °C for 10 h. To synthesize the hollow LMO NTs, the MnO_2 coated PCNFs were mixed with LiOH·H_2O in a molar ratio of 2:1. This mixture was heated at 480 °C for 3 h and then 750 °C for 10 h in air giving hollow LMO NTs. For comparison, some LMO nanoparticles were fabricated using the above-mentioned method, but without the PCNFs template. Thus, we obtained LMO particles and three types of hollow LMO NTs formed by coating PCNFs with MnO_2 for 10, 30, and 60 min (referred to herein as P-LMO, H-LMO10, H-LMO30, and H-LMO60, respectively).

2.2. Characterization

The morphological properties of the samples were determined by field emission-scanning electron microscopy (FESEM; Hitachi S-4800) and transmission electron microscopy (TEM; JEOL, 2100F, KBSI Suncheon Center). The crystal structures and chemical bonding states were determined by X-ray diffraction (XRD, RigaKu D/MAX2500V) with Cu Kα radiation in the angular range of 10°–90° with a step size of 0.02° and X-ray photoelectron spectroscopy (XPS, ESCALAB250) with an Al Kα X-ray source under a base pressure of 267 nPa, respectively. The electrochemical performance of the samples was investigated using Li coin cells (CR2032, Hohsen Corporation). The Li coin cells were composed of Li metal foil (Honjo Chemical, 99.8%) as the anode, the prepared samples as the cathode, a porous polypropylene membrane (Celgard 2400) as the separator, and a 1.0 M LiPF$_6$ solution in a mixture of ethylene carbonate and dimethyl carbonate (1:1) as the electrolyte. To fabricate the cathodes, slurries of the prepared samples

(70 wt%) as active material, ketjen black (10 wt%, Alfa Aesar) as a conducting material, and poly (vinylidene difluoride) (20 wt%) as a binder in N-methyl-2-pyrrolidinone solvent (NMP, Aldrich), were coated onto an Al foil substrate (aluminum foil, 15 μm). This was then dried at 100 °C for 12 h. The Li coin cells were assembled in a high-purity argon-filled glove box (<5 ppm, H_2O and O_2). The electrochemical impedance spectroscopy (EIS) measurements were performed in fresh cells over a frequency range of 100 kHz to 10 mHz at an AC signal strength of 5 mV. The galvanostatic charge-discharge measurements were performed using a WMPG 3000 battery cycler system (WonATech Corp., Korea) over a potential range of 3.3–4.3 V (versus Li/Li$^+$) at 25 °C. The cycle number dependence was measured up to 100 cycles at a current density of 1 C (120 mA g^{-1}). The rate performance of all the samples was investigated at C-rates of 1 C, 3 C, 5 C, 7 C, and 10 C before testing again at 1 C.

3. Results and discussion

Fig. 1 shows a schematic of the synthesis of hollow LMO NTs. As shown in Fig. 1a, the PCNFs were synthesized by electrospinning using a mixed solution of PAN and SAN polymers. The resultant PCNFs have micro-pores resulting from decomposition of the added SAN polymers during stabilization, which gives the enhanced surface area required to form a uniform MnO_2 shell [17]. Then the MnO_2 coating of the above-mentioned PCNFs was added by direct redox reaction (Fig. 1b). The MnO_2 coating on the PCNFs was used as the main matrix to form the LMO phase by a solid-state reaction using LiOH·H_2O, as shown by the following equation [18].

$$2n \ Mn^{IV}O_2 + n \ LiOH \rightarrow n \ LiMn^{III}Mn^{IV}O_4 + n/2 \ H_2O + n/4 \ O_2$$
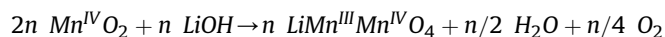
Combustion of the PCNFs generates the hollow core of the nanostructures, resulting in the formation of hollow LMO NTs (Fig. 1c). Thus, we successfully synthesized hollow LMO NTs by a three step process consisting of electrospinning, direct redox reaction, and solid-state reaction.

Fig. 2a–d shows the FESEM images of P-LMO, H-LMO10, H-LMO30, and H-LMO60. The morphology of P-LMO shows diameters in the range of ~0.83–~1.77 μm resulting from irregular aggregation. On the other hand, H-LMO10, H-LMO30, and H-LMO60 are observed as hollow nanotubes with holes ~210.3–231.5 nm in diameter. The formation of this nanostructure is induced by the combustion of the PCNFs during the solid-state reaction. The diameters and shell thicknesses of the hollow NTs are observed to be ~443.9–526.4 nm and ~77.0–113.3 nm for H-LMO10, ~474.4–526.4 nm and ~116.4–157.3 nm for H-LMO30, and ~513.2–583.5 nm and ~156.2–203.3 nm for H-LMO60, respectively. Their diameters and shell thicknesses increase with the thickness of
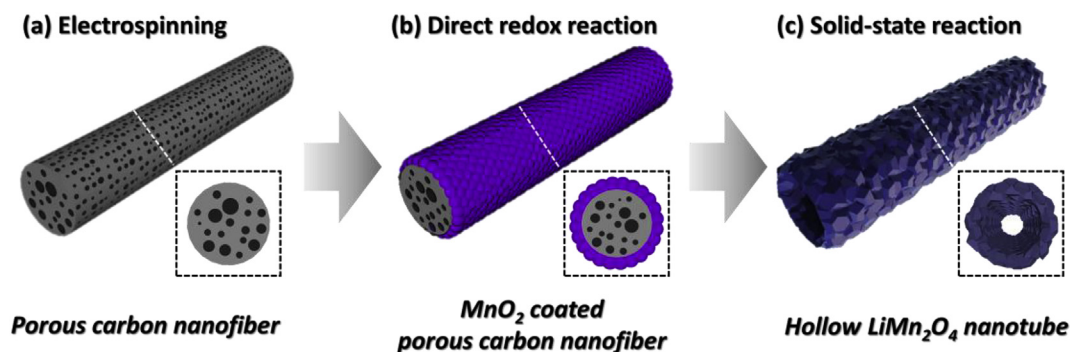

(a) Electrospinning   **(b) Direct redox reaction**   **(c) Solid-state reaction**

Porous carbon nanofiber   *MnO$_2$ coated porous carbon nanofiber*   *Hollow LiMn$_2$O$_4$ nanotube*

Fig. 1. A schematic illustration of process steps to fabricate the hollow LMO nanotubes.