



Design and synthesis of tube-in-tube structured NiO nanobelts with superior electrochemical properties for lithium-ion storage

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HIGHLIGHTS

- Novel 1-D tube-in-tube structured NiO nanobelts were synthesized by electrospinning process.
- Influence of calcination temperature on the formation of nanobelts with various morphologies was investigated in detail.
- The chemicals that optimized surface tension and viscosity of the aqueous solution enabled stable electrospinning process.
- Unique structured NiO tube-in-tube nanobelts showed excellent lithium-ion storage performances.

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ABSTRACT

Novel 1-D tube-in-tube structured NiO nanobelts were prepared by electrospinning process and subsequent one-step thermal treatment process. Nanobelt structured 1-D composite was electrospun from an aqueous solution containing poly(vinylpyrrolidone), citric acid, and dextrin which synergistically contributed to morphology control. The chemicals that optimized surface tension and viscosity of the aqueous solution enabled stable electrospinning process. Especially, dextrin played an important role in stable nanobelt formation due to its hygroscopic nature. During one-step oxidation process, the polymer composited nanobelt turned into carbon-free NiO@void@NiO tube-in-tube structured nanobelt by repeated combustion and contraction processes and Ostwald ripening mechanism. NiO tube-in-tube nanobelt prepared at 400 °C showed superior lithium-ion storage performances compared to those of NiO-C nanobelt and porous NiO nanobelt obtained at 300 and 500 °C, respectively. The discharge capacity of the tube-in-tube structured nanobelts after the 200th cycle at a current density of 1.0 A g⁻¹ was 992 mA h g⁻¹. Also, high discharge capacity of 531 mA h g⁻¹ at a current density of 10.0 A g⁻¹ proved its excellent power density. High structural stability and morphological benefits of tube-in-tube nanobelts resulted in superior lithium storage performance.

1. Introduction

Transition metal oxides have been widely studied as promising anode materials for lithium ion batteries (LIBs) because of their high capacities, which exceed those of commercial carbonaceous materials [1–9]. Among transition metal oxides, NiO has received great research interest for its low density, high abundance, and nontoxicity [10–14]. However, NiO has poor electronic conductivity like other transition metal oxides, which results in disturbance of conduction paths for both electron and Li⁺ ion [15–17]. These are considered as critical obstacles for LIBs and result in poor rate capability and cycling stability [15–17]. Therefore, various NiO materials with hollow and porous morphologies have been developed to achieve excellent electrochemical properties by

improving their structural stabilities during the repeated lithium insertion and deinsertion processes [18–26]. Kang et al. synthesized yolk-shell and single-crystalline NiO powders by continuous one-pot spray pyrolysis and flame spray pyrolysis, respectively [18]. Yolk-shell-structured NiO powders showed higher discharge capacity of 951 mA h g⁻¹ than that of the single-crystalline cubic NiO nanopowders (416 mA h g⁻¹) after 150 cycles. Synthesis of hierarchical 3D-NiO microspheres with ultra-thin porous nanoflakes by chemical co-precipitation method and subsequent thermal treatment was reported by Seo et al. [25]. The capacity of NiO microspheres retained 795 mA h g⁻¹ after 150 cycles at 0.5 C. Liu et al. synthesized highly ordered mesoporous NiO by a nanocasting method using mesoporous silica as the hard template [26]. The powders obtained using this

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method had specific capacity of 680 mA h g^{-1} after 50 cycles at 0.1 C, which was much higher than that of the commercial bulk NiO (188 mA h g^{-1}).

Recently, one-dimensional (1-D) nanostructures have been recognized as the most desirable materials for use in energy storage [27–35]. Their unique structures provide enhanced surface-to-volume ratios, short Li^+ ionic transport lengths, and efficient 1-D electron transport along their longitudinal directions [29,30]. Therefore, the application of 1-D geometries to the hollow nanostructure has been considered attractive for use in LIBs. Cho et al. prepared NiO nanofibers composed of hollow NiO nanospheres by electrospinning method and compared the lithium storage properties with those of porous NiO nanofibers [35]. The nanofibers composed of hollow nanospheres showed superior discharge capacity of 707 mA h g^{-1} than that of porous one (206 mA h g^{-1}) for the 250th cycle at a current density of 1.0 A g^{-1} .

This paper proposes a simple and highly efficient preparation method for NiO tube-in-tube-structured nanobelts by electrospinning process and subsequent heat-treatment process. To the best of our knowledge, preparation process for tube-in-tube-structured transition metal oxide nanobelts has not yet been researched. Also, there are not many reports on nanofibers electrospun from aqueous solution due to difficulty in obtaining the suitable degree of viscosity and surface tension. The first introduction of dextrin to aqueous electrospinning solution enabled the formation of nanobelt due to its hygroscopic nature. Addition of poly(vinylpyrrolidone) increased viscosity and lowered surface tension. Citric acid further lowered surface tension to a certain degree suitable for stable electrospinning. During subsequent oxidation, sudden combustion of carbonized electrospun nanobelt turned it into NiO-C@void@NiO fiber-in-tube morphology. Continuous heating yielded NiO tube-in-tube structure by Ostwald ripening. Electrochemical properties of tube-in-tube structured NiO nanobelts were compared with those of filled NiO-C nanobelt and porous NiO nanobelts prepared at different post-treatment temperatures.

2. Experimental

2.1. Synthesis of NiO nanobelts with tube-in-tube structure

NiO nanobelts with tube-in-tube structure were prepared using electrospinning process and subsequent thermal-treatment. First, composite nanobelts comprising nickel(II) nitrate tetrahydrate [$\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Junsei, 98.0%], poly(vinylpyrrolidone) [PVP, Mw: 1,300,000, Sigma Aldrich], citric acid [$\text{C}_6\text{H}_8\text{O}_7$, Samchun Chemicals, 99.5%], and dextrin [$(\text{C}_6\text{H}_{10}\text{O}_5)_n$, Samchun Chemicals] were electrospun. The electrospinning precursor solution was prepared by dissolving 2.0 g of PVP and 10.0 g of dextrin in a mixed solution containing 20 mL of deionized water and 2.0 g of citric acid with vigorous stirring for 3 h. Then, 3.0 g of nickel(II) nitrate tetrahydrate was added to the above solution. The prepared solution was loaded into a plastic syringe equipped with a 27-gauge stainless steel nozzle. The solution was subsequently ejected at a flow rate of 0.1 mL h^{-1} and electrospun onto a drum collector constantly heated at 180°C . During the electrospinning process, the distance between the tip and the collector was maintained at 15 cm, while the rotation speed of the drum was 150 rpm. The applied voltage between the collector and the syringe tip was 25 kV. The resulting nanobelts comprising $\text{Ni}(\text{NO}_3)_2$ -PVP-dextrin-citric acid were stabilized at 100°C under air for 3 h. Subsequently, the nanobelts were heat-treated at 300, 400, and 500°C for 3 h under air atmosphere. For simplicity, the resulting NiO nanobelts obtained after heat-treatment at 300, 400, and 500°C are referred to as “NiO/C-300”, “NiO-400”, and “NiO-500” respectively.

2.2. Characterization techniques

The microstructures of the samples were examined by field-emission scanning electron microscopy (FE-SEM, ULTRA PLUS, ZEISS) and field-

emission transmission electron microscopy (FE-TEM, JEOL, JEM-2100F). In addition, their phase analysis was evaluated by X-ray diffractometry (XRD, D8 Discover with GADDS, The Bruker) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The Fourier transfer infrared (FT-IR) spectra were obtained by a JASCO FT-IR 480 Plus spectrophotometer. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) with a focused monochromatic $\text{Al K}\alpha$ at 12 kV and 20 mA was used to analyze the composition of the specimens. The surface areas of the nanobelts were measured using the Brunauer–Emmett–Teller (BET) method using N_2 as the adsorbate gas. Thermogravimetric (TG) analysis was performed using a Pyris 1 TGA (Perkin Elmer) within a temperature range of $25\text{--}700^\circ\text{C}$ at a heating rate of $10^\circ\text{C min}^{-1}$ under air.

2.3. Electrochemical measurements

The capacities and cycle properties of the samples were measured using 2032-type coin cells. The cell electrodes were prepared using slurry consisting of 70 wt% active anode material, 20 wt% carbon black (Super-P) as a conductive material, and 10 wt% binder composed of sodium carboxymethyl cellulose (CMC) on a copper foil. Lithium metal and microporous poly(propylene) film were used as the counter electrode and separator, respectively. The electrolyte was created by dissolving 1 M LiPF_6 in a mixture of fluoroethylene carbonate and dimethyl carbonate (FEC/DMC, 1:1 v/v). The entire cell was assembled in an argon atmosphere in a glove box. The charge/discharge characteristics of the samples were measured at various current densities in the voltage range of 0.001–3.0 V. The size of the negative electrode containing the NiO nanobelts was $1.4 \text{ cm} \times 1.4 \text{ cm}$, and the mass loading was approximately 0.84 mg cm^{-2} . Cyclic voltammetry measurements were performed at a scan rate of 0.1 mV s^{-1} between 0.001 and 3.0 V. Electrochemical impedance spectra of NiO nanobelts were analyzed in the frequency range between 100 kHz and 10 MHz at room temperature with a signal amplitude of 5.0 mV.

3. Results and discussion

Morphologies of the as-spun composite electrospun from aqueous solutions containing nickel salt with PVP, dextrin, citric acid, and PVP/citric acid are shown in Fig. 1. In this study, in order to obtain uniform nanobelts, effects of each additive and their combination on morphology control during electrospinning process were demonstrated in detail. Fig. 1a shows the nickel salt-polymer composite without specific morphology, electrospun from aqueous solution containing PVP. It is generally known that surface tension of electrospinning solution should be lowered to fabricate 1-D morphology without bead formation. When PVP is dissolved in water, surface tension decreases slightly while viscosity rises. In order to obtain low enough surface tension for electrospinning by dissolving PVP in distilled water, it must be accompanied by a large increase in viscosity that blocks the stable electrospinning process [36,37]. In case of aqueous solution containing 10 wt % PVP, capillary breakup of electrospinning jets occurred due to high surface tension of the solution. As a result, droplets were generated and solidified on the drum collector surface, forming composite with random morphology. In search of organic compound that can lower the surface tension effectively, dextrin was chosen as a candidate [38]. In Fig. 1b, random morphology was observed for the nickel salt composite electrospun from a solution containing dextrin. Dextrin is highly soluble in water and contains many functional groups with ability to form hydrogen bonding with water. As a result, existence of dextrin blocks the formation of hydrogen bonding between water molecules, and thus can lower the surface tension. However, viscosity increase was not possible for dextrin is an oligomer with low molecular weight. It was not viscous enough and resulted in random shape. Electrospun nickel salt composite from aqueous solution containing citric acid is presented in Fig. 1c. Citric acid plays the role of lowering surface tension to some extent [39]. However, it does not satisfy the required viscosity and

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