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Spray deposition of $LiMn_2O_4$ nanoparticle-decorated multiwalled carbon nanotube films as cathode material for lithium-ion batteries

H.P. Hong [a], M.S. Kim [b], Y.H. Lee [c], J.S. Yu [b], C.J. Lee [d], N.K. Min [a,*]

[a] Department of Control and Instrumentation Engineering, Korea University, Jochiwon, 339-700, Republic of Korea
[b] Department of Advanced Materials Chemistry, BK21 Research Team, Korea University, Jochiwon, 339-700, Republic of Korea
[c] Department of Biomicrosystem Technology, Korea University, Seoul, 136-701, Republic of Korea
[d] School of Electrical Engineering, Korea University, Seoul, 136-710, Republic of Korea

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ABSTRACT

We prepared $LiMn_2O_4$ nanoparticle-decorated multiwalled carbon nanotube (MWCNT) films as a cathode electrode for lithium-ion batteries using a spray-deposition method. The surface morphologies and structures of the films were characterized using scanning electron microscopy and X-ray diffraction analysis. The results revealed that fairly homogeneous spinel $LiMn_2O_4$ nanopowder-based films with the grain size of 20–50 nm were successfully formed on the surface of the MWCNTs. Cyclic voltammetry confirmed the presence of typical spinel $LiMn_2O_4$ structure on the MWCNTs with showing stronger oxidative peaks of better reversibility as compared to a pure $LiMn_2O_4$ electrode. The spray-deposited $LiMn_2O_4$-decorated MWCNT film was also found to have a higher discharge capacity (97.2 mAh/g) than the as-deposited $LiMn_2O_4$ film (75.2 mAh/g) as well as excellent cycling stability. These characteristics are due to the fact that MWCNTs provide the cathode with multiple electron tunneling pathways and a mechanically strong framework.

1. Introduction

Rechargeable lithium ion (Li-ion) batteries are now widely used as the main power source for portable consumer electronics, medical devices, hybrid electric vehicles, etc., because of their superior energy density. Most of commercial lithium ion batteries consist of a graphite negative electrode (referred to as anode), a non-aqueous liquid electrolyte, and a lithium metal oxide positive electrode (referred to as cathode). The anode is generally one of three materials: lithium cobalt oxide ($LiCoO_2$), lithium manganese oxide ($LiMn_2O_4$), or lithium iron phosphate ($LiFePO_4$). The electrolyte is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complexes of lithium ions. Depending on materials choices, the voltage, capacity, life, and safety of a Li-ion battery can change dramatically. Although these batteries are commercially successful, we are reaching the limits in performance using the current electrode and electrolyte materials. For new generations of rechargeable Li-ion batteries, intensive research efforts have been made to develop new electrode materials or to design novel structures of electrode materials, including nanomaterials such as $LiFePO_4$ nanoparticles, $LiMn_2O_4$ nanorods, V_2O_5 nanotubes, $LiCoO_2$ nanowires, and Si–C nanocomposites.

While many new high-voltage and/or safer positive electrode materials have been successfully developed and commercialized in the last years, such as carbon-coated nano-$LiFePO_4$, [1–3] $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ [4,5], and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ [6,7], the replacement of the carbon graphite negative electrode has been relatively less successful.

Recently, carbon nanotubes (CNTs) have been employed as the alternative anode material in lithium ion batteries [8,9]. The purified single-walled CNTs showed a reversible capacity significantly higher than the capacity for graphite. However, the significantly high irreversible capacities and voltage hysteresis, as well as the absence of voltage plateau observed in all single-walled CNT materials, have limited the application of CNTs as the electrode material in lithium ion batteries [10]. More recently, CNT composite cathode electrodes are developed [11]. Composite cathode electrodes are not easy to fabricate by conventional deposition methods such as radio frequency sputtering, pulsed laser deposition, or chemical vapor deposition because these processes tend to destroy additives such as carbon black, CNTs, and oxide compounds. Other available methods for composite cathode, e.g., spin coating and doctor blade processes require a binder to interconnect metal oxide powder/additives. However, binders are electrically resistive organic polymers that cause degradation of battery capacity due to voltage drop by interfering electron transport in the cathode. Therefore, binder-free deposition methods are required for the composite cathode electrode fabrications.

Herein, we describe the fabrication of a $LiMn_2O_4$ nanoparticle-decorated MWCNT films as a cathode electrode material for Li-ion batteries using a spray-deposition method. Direct spray deposition of $LiMn_2O_4$ nanoparticle/MWCNT composites on current collectors has many advantages over conventional deposition methods. Spray deposition is suitable for mixed solutions and less complicated to prepare the film on current

* Corresponding author. Tel.: +82 2 925 2296.
E-mail address: nkmin@korea.ac.kr (N.K. Min).

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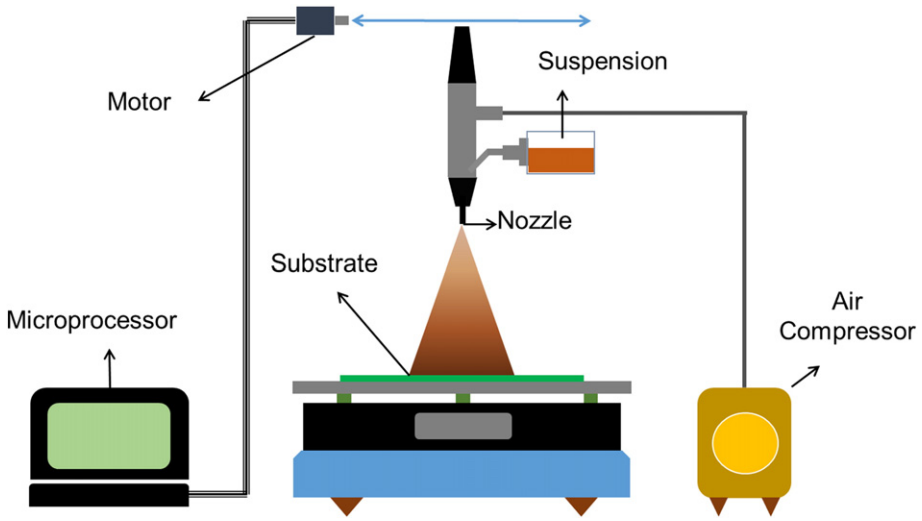

Fig. 1. Schematic of the spray-deposition equipment used to deposit film.

collectors than the sol–gel methods. More importantly, spray deposition does not require the preparation of powder because $LiMn_2O_4$ particles are deposited on the current collector with additives during the spraying process. In this report, spray-deposited $LiMn_2O_4$ nanoparticle/MWCNT composites were found to have significantly enhanced rate capacities and cycle performance due to the fact that MWCNTs have low resistivity, large surface area, and high physical strength.

2. Experimental details

2.1. Synthesis of solutions

We prepared two solutions: (a) $LiMn_2O_4$ (LM) and (b) $LiMn_2O_4$ nanoparticle-coated MWCNTs (LM-coated MWCNTs) in order to deposit the two kinds of cathode films. Anhydrous manganese acetylacetonate ($Mn(CH_3COCHCOCH_3)_3$), lithium acetylacetonate ($LiCH_3CO–CHCOCH_3$), 1-butanol, and acetic acid were purchased from Sigma-Aldrich. MWCNTs were purchased from Hanwha Nanotech Co. Ltd. (Korea) and were used without further purification.

The LM/MWCNT composite solution was made by mixing the precursors, manganese acetylacetonate, and lithium acetylacetonate, with MWCNTs in 1-butanol:acetic acid 3:1 v/v. The concentrations of a precursor were adjusted to a 1:2 molar ratio of Li to Mn. Prior to dissolving the solutes in the solvent, MWCNTs (13.6 mg) were dispersed in 1-butanol (30 mL) using tip sonication for 20 min. This LM/MWCNT composite solution (0.03 M) was stirred with a magnetic stirrer under nitrogen atmosphere for 5 h to ensure homogenous dispersion. The MWCNT content was maintained at 10 wt.%. For comparison, a LM solution without MWCNTs was also prepared.

2.2. Fabrication of $LiMn_2O_4$ nanoparticle-coated MWCNT films and electrochemical test cells

Fig. 1 shows a schematic of the spray deposition system using for this work consisting of a nozzle, actuators, microprocessor, air compressor, and heating plate. The films were spray-deposited on the preheated stainless steel substrates (SST304, 100 μm thick; Nilaco Corp., Japan). To avoid a decrease of substrate temperature and forming uniform films during deposition, dual axis control spray method was used. By constantly moving a nozzle over predefined area, we got good quality thin films. The spray process was done in 50 cycles at 240-s intervals, and the spray time was 22 s/cycle. The optimized conditions of film formation are described in Table 1.

Sequentially, as-deposited films were dried in a tube furnace at 360 °C for 1 h in order to combust the organic components. After drying, the amorphous LM-coated MWCNT films were decomposed in a furnace at 380 °C for 6 h and, subsequently, annealed at 650 °C for 30 min in ambient atmosphere. The rate of temperature change, both increasing and decreasing, was fixed at 1.5 °C/min. Annealing processes are essential because crystalline LM exhibits better performance with regards to cyclability and rate capacity than amorphous LM.

The electrochemical performance of prepared films was investigated using coin cells (CR2032) with lithium foil as counter and reference electrodes. The working electrodes were fabricated by spraying the precursor solutions on round SST304 current-collectors 15 mm in diameter and 100 μm thick. The weight of cathode materials was assessed by weighing the substrate before and after spray-depositing the solutions (1.8–2.0 mg). The assembly of the cells was done in a dry, argon-filled glove box. A Cellgard 2400 microporous polypropylene film was used as a separator. The electrolyte was 1 M $LiPF_6$ dissolved in a 1:1 v/v mixture of ethylene carbonate and ethylmethyl carbonate.

Table 1
Optimum spray conditions for LM-coated MWCNT film deposition.

Flow rate	0.68 mL/min
Substrate temperature	360 °C
Sprayed area	25 mm^2
Distance between the nozzle and substrate	9 cm

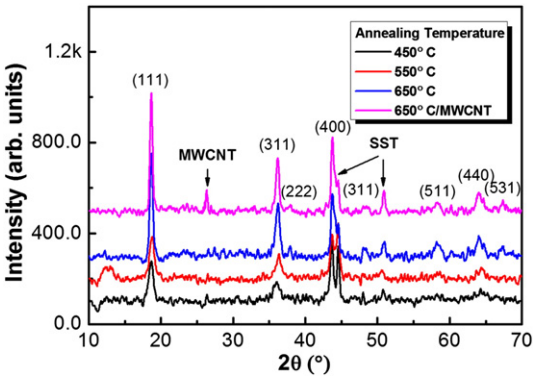

Fig. 2. XRD patterns of samples prepared by spray deposition (a) without MWCNTs and (b) with MWCNTs depending on annealing temperature.