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Carbon nanotube web-based current collectors for high-performance lithium ion batteries

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ABSTRACT

In lithium-ion batteries, electrodes with well-defined three-dimensional (3D) nanostructure electrodes commonly possess improved lithium ion mass transport, stable cyclability, and excellent high rate performance. In this study, we demonstrate the 3D electrode consisting of web-type carbon nanotube (CNT-web) and $LiNi_{0.4}Mn_{0.3}Co_{0.3}O_2$ (NMC-433) as a cathode for high-performance lithium-ion batteries. The as-prepared three-dimensional nanostructure electrode (web-NMC) contains the CNT-web, which has a highly crystalline structure containing networks of individual nanotubes, and NMC-433 with a well-defined structure and composition. The web-NMC exhibits enhanced electrochemical reaction properties of lithium ions such as high specific capacity ($\sim$150 mAh g^{-1}), high rate cycling performance, and capacity retention (48%) due to an efficient electron transport path and fast lithium ion transport compared with the conventional structure electrode.

1. Introduction

Flexible energy storage devices have attracted growing attention with the fast development of bendable electronic systems. Rechargeable lithium ion batteries (LIBs) have shown great promise as flexible power sources due to their high operating voltage, high-energy capacity, and long-term cyclability [1,2]. These devices can be flexible, lightweight, and manufactured through a low cost, roll-to-roll printing process, which can be directly integrated into the flexible substrates for the easy of system integrations [3–6]. Recently Arico et al. reported that they fabricated an all-solid-state bendable LIB using a new universal transfer approach based on sacrificial mica substrates [1]. Toward an all-in-one flexible system, the development of a bendable high-power source that can be applied to consumer electronics has been an obstacle to overcome. Traditional LIBs are key components for the development of portable, entertainment, computing and telecommunication equipment due to their relatively high specific energy and specific power [7]. These batteries are based on electrode reactions using classical intercalation reactions for which Li^+ ions are inserted/extracted from active materials that are applied on the current collectors, with Al for the positive electrode and Cu for the negative electrode [8,9]. In a conventional lithium ion cell, the power density is limited by the poorly conducting pathways by the poor electronic conductivity of the active material, poor ionic conductivity of the electrolyte to the active material surface at high charge/discharge rates, and the poorly conducting pathways from the bulk electrode to the metallic current collector [10–12].

Commercial LIBs contain $LiPF_6$ salt in their electrolyte solution, which contains water as an impurity below tens of ppm level. Although the quantity of the water is negligible, it accelerates the decomposition of the $LiPF_6$ salt at elevated temperatures (>40 °C) and at high potentials (>4 V vs. Li/Li^+) [8,13,14]. When the salt is decomposed, HF is produced as a byproduct. The formed HF reacts with the positive electrode materials, resulting in the formation of water molecules, and, thus, ceaselessly decomposing the $LiPF_6$ salt. Although metallic current collectors are passivated under alkyl carbonate solutions containing $LiPF_6$ salt, the current collectors corrode during the lifetime of the cells due to their reaction with HF [15–17]. To overcome these impediments, the ideal electrode architecture that would provide efficient ion and electron transports consists of a three-dimensional interpenetrating network of electron and ion pathways, and initial strides have been made to fabricate such structures [10,11]. Copper pillar array

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[12], nickel network [18–20], polymer scaffold [21], and nanotube [22] carbonaceous interpenetrating structures have been fabricated to serve as conductive pathways in the cathodes and anodes of batteries. In particular, carbon nanotubes (CNTs) have been studied for battery applications due to their excellent electrical conductivity, large specific surface area, high mesoporosity, and good electrolyte accessibility. Initially, randomly entangled CNTs were used as host materials for direct Li^+ intercalation in anodes [23–25] or as conductive additives in composite electrodes with graphite [26–28]. For cathodes, CNTs were studied as conductive additives in composite electrodes with metal oxides [29,30] or as conductive substrates for metal oxide electrodes [31–33]. To date, for the synthesis of carbon nanotubes, attention has been focused on the post-processing of dispersed nanotubes by drying these materials to produce films [34,35], coupled with electric or magnetic fields [36]. Similarly, fibers of nanotubes [37] or liquid-crystalline spinning [38,39] have also been drawn or spun from solutions or gels, but their assembly into continuous fibers has only been achieved through post-processing methods. Li et al. reported on carbon nanotubes that were directly made from the chemical vapor deposition (CVD) synthesis zone of a furnace using a liquid source of carbon and an iron nano catalyst [40]. In this work, carbon-nanotube web-based nanostructure electrodes were prepared using the direct spinning method for high-performance LIBs. The carbon-nanotube web-based electrodes delivered a high reversible capacity, as well as demonstrated a good capacity retention after cycling and, high reversible capacity, even at high C rate discharging.

2. Experimental

To prepare the $LiNi_{0.4}Mn_{0.3}Co_{0.3}O_2$ electrode, $(Ni_{0.4}Mn_{0.3}Co_{0.3})\cdot(OH)_2$ was synthesized from $NiSO_4\cdot 6H_2O$ (99.999%, Aldrich), $MnSO_4\cdot H_2O$, and $CoSO_4\cdot 7H_2O$ (99%+, Aldrich) using a co-precipitation method (denoted as NMC-433). A stoichiometric amount of each material (Ni:Mn:Co = 0.4:0.3:0.3) was dissolved in purified water and kept for 48 h at room temperature to obtain the slurry contained a metal hydroxide. The obtained metal hydroxide powder was heated at 300 °C for 12 h and then mixed with the lithium salt at a stoichiometric ratio of 4:3:3. The mixture was calcined at 950 °C for 24 h and recalcined at 500 °C for 24 h in order to obtain the resulting the powder.

The solution used to synthesize the web-type carbon nanotubes (denoted as CNT-web) was prepared by mixing acetone 98.0 wt%, ferrocene 0.2 wt%, thiophene 0.8 wt%, and polysorbate_20 1.0 wt%. The solution was injected at a rate of 10 ml h^{-1} with a hydrogen gas flow rate of 1000 SCCM (standard cubic centimeter per minute) into a vertical reactor heated to 1200 °C, and the synthesized CNT web was wound at 5 m min^{-1}. The CNT-web was heat-treated in a furnace at 1000 °C under a N_2 atmosphere for 30 min. The details of the apparatus used in the CNT-web synthesis were schematically described in our previous paper [41,42], and the detailed principle of the synthesis was previously described [35,38]. Acetone (99.7%) was purchased from Samchun Chemical (Korea). Ferrocene (98%), thiophene (99%), and polysorbate_20 were purchased from Sigma–Aldrich. The NMC-433 as an active material was dispersed in anhydrous ethanol by sonication. After 10-layer stacking of CNT-web, the NMC-433 as an active cathode material was injected at 0.5 ml across the CNT-web using a spray dry method. After repeating this process 18 times, finally, the web-NMC was wrapped with the CNT-web.

The size and shape of the electrodes were observed using a field emission scanning electron microscope (FE-SEM JSM-6700F, Eindhoven, Netherland). XRD analysis was carried out using a Bruker X-ray diffractometer with a Cu Kα (λ = 0.15418 nm) source and a Ni filter (D2 PHASER, Bruker AXS). The source was operated at 30 kV and 10 mA. The 2θ angular scan was performed from 10° to 80° at a scan rate of 0.5° min^{-1}. The carbon structure was characterized by Raman spectroscopy with the Red Light laser line at 514 nm (Horiba's LabRAM HR). The thermogravimetric analysis (TGA) curve was obtained in a thermal analyzer (TGA/DSC1 star, Mettler Toledo) in the range of 25–1000 °C at a heating rate of 10 °C min^{-1} with an air flow of 60 cm^3 min^{-1}.

To assemble the lithium coin cells (size 2032, Hohsen Corporation), the NMC-433 with the CNT-web was used as a working electrode and evaluated with respect to the lithium foil (FMC Corporation) as a counter electrode. The conventional coin cell was assembled using the NMC-433 casted on the Al foil (denoted as c-NMC). The electrodes were fabricated by mixing 80 wt% NMC-433 with 10 wt% polyvinylidene difluoride (PVDF) binder, and 10 wt% ketjen black as a conducting agent in 1-methyl-2 pyrrolidinone (NMP). The mixed slurry was cast onto an Al foil as a current collector and dried in air at 100 °C for 12 h. The web-NMC coin cell was assembled using the NMC-433. The electrodes, with an area of 1.32 cm^2, were dried at 70 °C in a vacuum oven. The coin cells were assembled inside an argon-filled glove box (<5 ppm, H_2O and O_2). The electrodes of the cells were separated by a porous polypropylene membrane (Celgard 2400) with an electrolyte solution consisting of 1.1 M $LiPF_6$ in (ethylene carbonate:dimethyl carbonate) = (1:1) as the solvent mixture (Soulbrain Co., Ltd.).

After assembling coin cells, the charge–discharge cycling was performed on a multichannel battery tester (WBCS300L, Wonatech Co.). The cells were cycled between 2.5 and 4.2 V vs. Li/Li^+ at various currents with a 30-min rest period between each charge (galvanostatic and potentiostatic mode)/discharge (galvanostatic mode) half cycle at a constant temperature of 25 °C. The activated materials were tested for 10 cycles at 150 mA g^{-1}, followed by 10 cycles of 300, 750, 1500, 3000 mA g^{-1}, and then for 10 cycles at 150 mA g^{-1} to evaluate the high rate cycling performance. Electrochemical impedance spectroscopy measurements (EIS) were performed on the AUTOLAB electrochemical workstation by applying an AC voltage of 5 mV amplitude over the frequency range 100 kHz–0.01 Hz. The impedance spectroscopic measurement of the cells were carried out by charging at 4.2 V.

3. Results and discussion

CNT-web was synthesized by injecting a raw material solution and hydrogen gas from the top of the hot vertical furnace (Fig. 1(a)). The raw material solution consists of thiophene (catalyst), ferrocene (co-catalyst), and acetone (carbon source). Ferrocene was decomposed by thermal energy, and iron particles were released; the sulfur that was released from thiophene had the role of active agent, and the iron-sulfide formed from these reactions. The carbon that was supplied by the decomposition of the acetone was diffused into the iron-sulfide, becoming saturated; the carbon nanotubes were deposited during this reaction via an iron catalyst. If a solution was supplied inside the hot furnace carbon nanotube assemblies were formed and drawn out in response to the winder. As shown in the synthesized CNT-web (Fig. 1(b)), the NMC-433 was injected across the CNT-web with a thickness of 10 layers using a spray dry method. Finally, the as-prepared nanostructure electrode consisted of the CNT-web and NMC-433 with a thickness of ~180 layers (denoted as web-NMC). In contrast, in the typical LIBs, an active material was casted on an aluminum current collector. In the as-formed web-NMC, the carbon nanotube bundles having a diameter of 30 nm were present to form a network containing the NMC-433 (Fig. 1(c) and (d)). The CNT-web based nanostructure electrode is even flexible in liquid nitrogen as presented in the previous study [42]. The web-NMC composed of the NMC-433 as an active material