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Design and Tailoring of a Three-Dimensional Lithium Rich Layered Oxide-Graphene/Carbon Nanotubes Composite for Lithium-Ion Batteries

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ABSTRACT

Poor rate capability and cycling performance are the major barriers to the application of lithium rich layered oxides as the next generation cathodes for lithium-ion batteries. In this paper, a novel tactics is applied to enhance the rate property and low temperature performance of lithium rich layered oxides materials by using graphene and multi-walled carbon nanotubes as the building blocks to form a hybrid 3D conductive network in the synthesized composites. Spray pyrolysis method is employed to obtain the target material. The hybrid 3D conductive network can decrease the reaction overpotential greatly, as well as reduce the cell resistance and enhance the lithium ion transportation in the bulk material, which are confirmed by cyclic voltammetry measurement and electrochemical impedance spectroscopy. The conductivity of the obtained composite is so high that no additional conductive agent is needed in the fabrication of electrodes. Our investigation further demonstrates that the conducting framework can efficiently alleviate the polarization of pristine lithium rich layered oxides material, leading to an outstanding enhancement in rate capability, low temperature performance and cycling stability.

1. Introduction

Recently, lithium-rich layered materials with a general formula of $Li_2MnO_3{\cdot}LiMO_2$ (M = Mn, Ni, Co) have attracted increasing interest, due to their high specific capacities (up to 250 mAh g^{-1}) [1,2]. However, the commercialization of those materials is currently hindered by some drawbacks the materials possessed, such as low rate capabilities [3], large voltage decay during cycling [4] and the irreversible capacity loss in the first charge/discharge process [5]. In particular, the poor kinetics is not only related to the Li_2MnO_3 component, lithium ion diffusion pathway, and interface reaction barrier [2], but also associated with the electronic and ion conductivity of $Li_2MnO_3{\cdot}LiMO_2$(M = Mn, Ni, Co) and electrodes [6]. Thus improving the electronic and ion conductivity of the bulk material is an effective way to decrease the electrochemical and concentration polarizations in the electrodes, which will be also helpful to depress the side reactions and enhance Li^+ transportation during the charge/discharge processes. Consequently an enhanced cycling performance and better high-rate capability can be expected.

As is all known, carbon nanotube (1D) [7,8] and graphene (2D) [9,10] are appealing building blocks of conductivity network for the purpose of resolving the issues of sluggish electron transport kinetics and rate performances. Many types of composite materials consisting of graphene (GN) or carbon nano-tubes (CNTs) have been synthesized and used in LIBs to take advantage of their superior electrical conductivity and mechanical flexibility, such as $Li_3V_2(PO_4)_3$ [11], $LiFePO_4$ [12,13], $LiMO_2$ [14,15], $LiMn_2O_4$ [16], $LiMnO_3$-$LiMO_2$ [6,17], and so on. Besides, hybridized GN and CNTs which have 3D conductive network for active materials are also proposed to enhance the electrochemical performance and flexible of active materials [18–20]. However, it is difficult to form high effective conductive network when using these materials, while GN or CNTs could be only loosely wrapped on the surface of the second particles [21]. Most primary particles inside the second particles still show poor kinetics and high polarizations in the obtained materials, resulting in limited enhancement in electrochemical activity of the whole materials [15,22]. Besides, GN can exhibit a steric hindrance effect for the Li^+ diffusion due to the

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planar structure [23,24]. So the homogeneous dispersion and good contact design between nano-carbon and active material is the key point in this issue.

Spray pyrolysis is an effective one-step production technique with advantages of short production time and homogenous particle composition in the final products [25,26]. Moreover, Spray pyrolysis is also an effective method in maintaining phase uniformity of the prepared materials due to the rapid evaporation of solvent in the synthesizing process, which is beneficial in forming isotropic capillary compression force to avoid the agglomeration of GN sheets and CNTs caused by van der Waals force [26].

In this work, we designed and prepared $0.5Li_2MnO_3 \cdot 0.5LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ (denoted as LR-NCM) composites with hybrid multi-walled CNTs and GN sheets conductive network by spray pyrolysis method. In our design, the LR-NCM primary particles were tightly wrapped with multi-walled CNTs and GN pieces (with the size of 1–3 μm) connect among particles of LR-NCM, as shown in Fig. 1. Hereafter, for simplification, we abbreviate the present double nano-carbon decorated LR-NCM composite as LR-NCM@CNT&GN, in which LR-NCM, CNTs and GN represent the LR-NCM primary particles, multi-walled carbon nano-tubes, and graphene sheets, respectively.

2. Experimental

2.1. Synthesis of LR-NCM

LR-NCM sample was synthesized by a Spray pyrolysis method combining with annealing. In a typical process, astoichiometric mixture of $Ni(Ac)_2 \cdot 4H_2O$, $Co(Ac)_2 \cdot 4H_2O$, $Mn(Ac)_2 \cdot 4H_2O$ and $LiOH \cdot H_2O$ (5%excess) were grounded for 2 h with de-ionized water as solvent. The resulting slurry was added into the spray drier machine by peristaltic pump with a speed of 1500 mL h^{-1} and atomized at 220 °C with atomizing pressure of 0.5 MPa. The obtained hollow spherical precursor was heated at 500 °C for 10 h and then sintered at 850 °C for 16 h.

2.2. Prepared LR-NCM@GN&CNT

In preparing the LR-NCM@GN&CNT composite, the as-prepared LR-NCM particles were firstly dispersed by ball-milling method, the sample was milled at a planetary ball mill with a speed of 300 rpm for 2 h using tungsten carbide vial and zirconium oxide balls. A ball to-mixture weight ratio was 30:1. Afterwards, 1600 g composite conductive aqueous solution NCL-O5 (GN:CNTs = 3:7 with 5.7% solid content from BTR Nano Tech. Co., Ltd.) was dispersed in 1.5 L water and, then 920 g dispersed of LR-NCM was added to the suspension and magnetically stirred at 50 °C for 4 h. The resulting slurry was added into the spray drier machine by peristaltic pump at 1500 $mL \cdot h^{-1}$ and atomized at 220 °C with atomizing pressure of 0.5 MPa. The as-obtained mixture was dried overnight at 120 °C.

2.3. Characterization

X-ray diffraction (XRD) measurements of the LR-NCM and LR-NCM@GN&CNT powder were performed using a Philips PW3710 with filtered Cu Kα radiation (Rigaku D/max-2500). Raman measurements were carried out using a DXR Raman Microscope (Thermao Fisher Scientific Inc.) with a laser wavelength of 514.5 nm. The morphology, size and the microstructures morphology of the LR-NCM powder and the LR-NCM@GN&CNT composite were investigated by Scanning electron microscopy (SEM; Hitachi S-4800) with an operation voltage of 5 kV and transmission electron microscopy (TEM; JEM-2100HR). Thermogravimetric analysis (TGA) curves were collected by using a Netzsch system with a heating rate of 5 °C min^{-1} in air. The four-point probe resistivity measurement system is used to measure the electronic conductivities of the LR-NCM powder and the LR-NCM@GN&CNT composite.

2.4. Electrochemical measurement

Electrochemical measurements were performed using Swageloktype cells assembled in an argon-filled glove box. A mixture of LR-NCM@GN&CNT and poly(vinyl difluoride) (PVDF) with a weight ratio of 90:10 was pasted on an Al foil to prepare the working electrodes. As a comparison, the electrode of LR-NCM was prepared by mixing active material, carbon black(CB) and poly (vinyl difluoride) (PVDF) with a weight ratio of 80:10:10 and Al foil was used as the current collector. The loading mass of active materials is about 10 mg cm^{-2}. Pure lithium foil was used as a counter electrode. Celgard 2502 (25 μm) was utilized as separator. The electrolyte consisted of a solution of 1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (3:7 in wt%) obtained from Guangzhou Tinci Materials Technology Co., Ltd. The cells were tested on a LAND-CT2001A battery test system (Jinnuo Wuhan Co., Ltd., P. R. China) with Galvano statically charged-discharged mode. Low temperature performance was tested in the voltage range of 2.0–4.8 V under a constant current density of 0.2C at various low temperatures (25, 0, −10 and −20 °C). Here, it is noted that the cycling at −20, −10 and 0 °C was conducted in a household refrigerator with about ±2 °C fluctuation. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out on an Autolab PG302 N at room temperature.

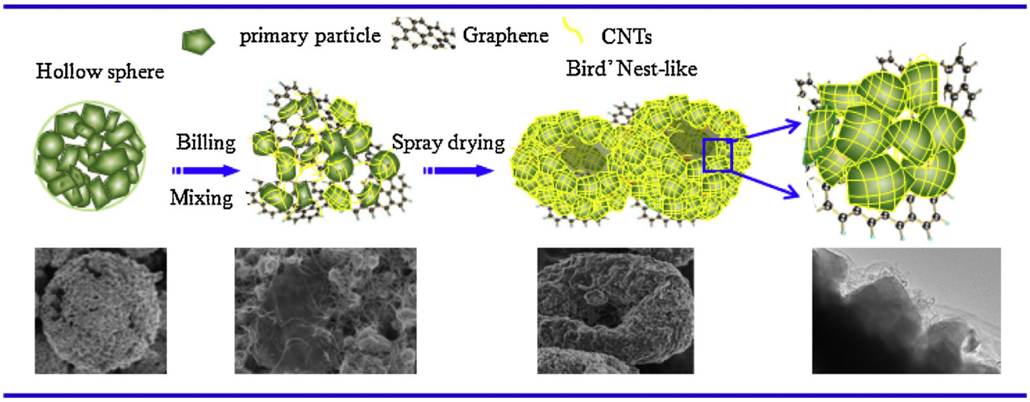

Fig. 1. Schematic illustration of the preparation process and the micro-scale structure of LR-NCM@GN&CNT composite.