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Free-standing and flexible $LiMnTiO_4$/carbon nanotube cathodes for high performance lithium ion batteries

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HIGHLIGHTS

- A free-standing cathode based on $LiMnTiO_4$ and multiwall carbon nanotube is developed.
- MWCNT networks improve reversible capacity and rate capability.
- $LiMnTiO_4$/MWCNT cathode exhibits the flexibility and light-weight.

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ABSTRACT

A flexible, free-standing, and light-weight $LiMnTiO_4$/MWCNT electrode has been prepared by vacuum filtration method for the first time. The as-prepared flexible $LiMnTiO_4$/MWCNT electrode possesses a three-dimensional braiding structure in which $LiMnTiO_4$ particles are well embedded in the twining CNT networks. The novel $LiMnTiO_4$/MWCNT electrodes show tensile strength of 1.34 MPa and 2.04 MPa, when the percentages of MWCNTs reach to 30% and 50%, respectively. This novel flexible electrode exhibits a superior electrochemical property, especially at rate capability and cycling stability. The $LiMnTiO_4$/MWCNT electrode can deliver capacity of 161 mAh g^{-1} (86.4% retention) after 50 cycles at 0.5C rate. Since the high conductivity from MWCNT networks, the $LiMnTiO_4$/MWCNT electrode can still maintain a capacity of 77 mAh g^{-1} at 5C rate, which is much higher than that of the conventional electrode fabricated by slurry casting method on Al foil. The features of free-standing, light-weight, and excellent electrochemical performance indicate the potential of using the $LiMnTiO_4$/MWCNT cathode in new-generation flexible lithium ion batteries.

1. Introduction

With rapid development in portable electronic devices such as mobile phone, flexible displays, ultra-thin laptop computer and wearable devices, higher demand in flexible energy storage applications has been raised to meet the energy requirements [1–3]. Due to the high power capability and durable cycle life, lithium ion battery is one of the most attractive and promising candidates compared with other battery technologies. However, except for meeting the ever-increasing energy density and rate capability, new requirements of lithium ion batteries, such as flexibility, high mechanical strength, and light-weight have been imposed to identify with the improvement of portable electronic equipment [4–6] and even the future electric vehicles [7]. Hence, developing the innovative lithium ion battery with flexibility and high power density is crucial for the challenges from new generation portable electronics.

In order to meet the above-mentioned requirements, optimizing the properties of electrode has been demonstrated as one of the most efficient approaches [8–10]. In terms of development of electrode materials, extensive efforts have been focused on developing novel cathode materials such as surface coating and element

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substitution [11]. For instance, the $LiMnTiO_4$ cathode material, which formed by substituting Ti^{4+} for Mn^{4+} in $LiMn_2O_4$, can provide higher capacity and excellent cycling stability than conventional cathode materials such as $LiCoO_2$ [12] and $LiFePO_4$ [13]. Besides, a new series of the titanate cathode material such as Li_2MTiO_4 (M = Mn, Fe, Co, Ni) has also emerged as a promising candidate for lithium ion batteries [14,15], which has a cubic cation disordered rock salt structure and offers a high theoretical capacity and stability. In terms of realizing the properties of light-weight and flexibility, the elimination of the inactive electrode components including polymer binder, conductive additive, and metal foil has been carried out in some reports [16]. On the one hand, it will be favorable to decrease the overall weight and have higher power density [17] in a binder-free electrode structure which contains more active materials. On the other hand, with the volumetric change [8,18,19] during charge/discharge processes, debonding will occur at the interface between electrode and current collector [20,21] in the traditional electrode structure, which is more serious in flexible batteries because of the bending and rolling activities [22]. It is quite clear that this issue will be automatically solved by an integrative electrode structure design.

Recently, many novel designs of electrode structure have been developed to keep the pace with the flexible lithium ion batteries [23–30]. For example, Lu et al. [24] developed an in-situ hydrothermal process to synthesize high performance $LiMn_2O_4$/CNT cathodes, which show good flexibility, high capacity and stable cycling performance. Lee et al. [26] developed the synthesis of free-standing, binder-free CNT anode electrodes of tens of microns in thickness by using the method of vacuum filtration. Wu et al. [31] provided the combination of $LiNi_{0.5}Mn_{1.5}O_4$ with multiwall carbon nanotube, which achieved electronical enhancement and light-weight electrode structure. Although these flexible electrodes can provide superior electrochemical performance, most of them are synthesized by sophisticated methods, which results in complexity during preparation process and decreases the feasibility in the battery industry. In addition, to the best of our knowledge, there are few reports about the application of Ti-substituted cathode material in flexible electrode.

In this study, we have synthesized the $LiMnTiO_4$ nanoparticles by the sol-gel method. In addition, MWCNT (purity 95%, diameter 15–60 nm) is purified and functionalized for good suspension. Then a novel free-standing, flexible, binder-free electrode design is developed by the integration of $LiMnTiO_4$ nanoparticles and MWCNT through simple vacuum filtration method. Meanwhile, the galvanostatic charge/discharge performance of $LiMnTiO_4$/MWCNT electrodes and mechanical performances are both studied.

As a free-standing cathode for lithium ion batteries, $LiMnTiO_4$/MWCNT electrodes are expected to have superior overall performances including high capacity, excellent rate capability, good cycle stability, lightweight, and flexibility. On the one hand, the substitution of Ti^{4+} for Mn^{4+} in $LiMn_2O_4$ can provide a higher bonding energy (Ti–O, 662 kJ mol^{-1}) than Mn–O (402 kJ mol^{-1}) [32], which reduces the concentration of Jahn-Teller Mn^{3+} ions. Furthermore, the Mn^{2+}/Mn^{4+} redox couple in $LiMnTiO_4$ contributes to a high theoretical capacity of 308 mAh g^{-1} [33]. On the other hand, the porous and twining MWCNT networks can promote electrolyte infiltration, which can accelerate both electrons and Li ions transformation. Without the inactive materials, the power density of entire electrode has been significantly improved compared with the conventional electrodes. Combining the above-mentioned advantages, the free-standing $LiMnTiO_4$/MWCNT electrode could be a promising candidate for new flexible lithium ion batteries.

2. Experimental section

2.1. Preparation of $LiMnTiO_4$/MWCNT electrodes

$LiMnTiO_4$ particles were synthesized using a well-known sol-gel method [34,35]. Stoichiometric amounts of lithium acetate dihydrate, manganese acetate tetrahydrate and tetra-*n*-butyl titanate were dissolved in ethanol, and refluxed at 353 K for 24 h with continued vigorous stirring until a transparent sol was obtained. After that, the resultant sol was dried at 393 K for 12 h under air atmosphere. Finally, the mixture was hand-milled in an agate mortar and sintered at 923 K for 10 h in air.

The purified and functionalized MWCNTs dealt by means of the mild acid treatment process (see Supplementary data) were dispersed in DI water with Triton X-100 (2.5 ml) as the surfactant to form a stable suspension with probe-sonication. $LiMnTiO_4$ powders were added to about 70% of the as-prepared MWCNT suspension and dispersed by the ultrasonic force again.

$LiMnTiO_4$/MWCNT electrodes were then prepared by vacuum filtration. About 15% of the as-prepared MWCNT suspension was filtered first through a porous membrane, the Celgard 3500 polypropylene separator, to obtain a thin MWCNT bottom layer. The mixture of $LiMnTiO_4$/MWCNT suspension was added to form a middle layer before covering another MWCNT layer on the surface. To remove the surfactant residue thoroughly, the resultant $LiMnTiO_4$/MWCNT film was washed with DI water (1000 mL), followed closely by methanol (100 mL). During the last step, the film was dried in a vacuum chamber at 353 K for 72 h. The $LiMnTiO_4$/MWCNT electrodes with two weight percentages of MWCNTs, 30% and 50%, were both obtained in this work.

2.2. Material characterization

Structural and crystallographic analysis of the as-prepared materials was determined by X-ray diffraction (XRD) using a Rigaku SmartLab diffractometer with a Cu-Kα radiation. The Fourier transform infrared (FTIR) spectra were recorded to confirm presence of the functional groups in the multi-walled carbon nanotubes structure, using a NEXUS670 Fourier transform spectrometer (NICOLET, USA) over the range of 4000–400 cm^{-1} at room temperature. The morphologies of the samples were characterized by a field emission scanning electron microscope (HITACHI S-4800). The $LiMnTiO_4$/MWCNT films were cut into rectangular strips of approximately 4 mm × 30 mm for testing. Static mechanical tests [36–38] were carried out on a Hounsfield (HS5N) tensile tester with a strain rate of 0.05 mm min^{-1}.

2.3. Electrochemical measurements

The electrochemical performance was evaluated using CR2032-type coin cells. The $LiMnTiO_4$/MWCNT film was cut into small pieces with 12 mm diameter. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 by volume). For comparison, conventional electrodes were made by slurry casting method on Al foil. The weight ratio was $LiMnTiO_4$: carbon black: polyvinylidene fluoride = 8: 1: 1. Galvanostatic charge/discharge testing was performed between 1.5 and 4.8 V at 298 K by a BT-2000 battery testing system (Arbin, USA). The cyclic voltammetry (CV) was measured using the CHI 660D electrochemical workstation in the voltage range of 1.5 V–4.8 V at the scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectra (EIS) was tested at a frequency range from 0.01 Hz to 10^5 Hz with an amplitude of 5 mV.